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The influence of atmospheric sulphur emissions on nutrient return via throughfall and stemflow in three boreal forest ecosystems

by

© Ross Wadsworth Parker

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

DEPARTMENT OF FOREST SCIENCE

EDMONTON, ALBERTA

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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled The influence of atmospheric sulphur emissions on nutrient return via throughfall and stemflow in three boreal forest ecosystems submitted by Ross Wadsworth Parker in partial fulfilment of the requirements for the degree of Master of Science in Forestry.

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Date October 6 1978

DEDICATION

To my parents, in appreciation of their encouragement and support given to me.

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TABLE OF CONTENTS

	page
ACKNOWLEDGEMENTS	v
LIST OF TABLES	x
LIST OF FIGURES	xvi
LIST OF PLATES	xviii
ABSTRACT	xix
1. INTRODUCTION	1
2. LITERATURE REVIEW	6
2.1 Nutrient Inputs	6
2.2 Distribution of Precipitation Under Forest Stands	9
2.3 Leaching of Nutrients From Tree Crowns	11
2.3.1 Nature of the Leaching Process	16
2.4 Nutrient Content of Litter	24
3. MATERIALS AND METHODS	26
3.1 Description of the Study Area	26
3.2 Nutrient Cycling Study	26
3.2.1 Experimental Design	29
3.2.2 Plot Description	34
3.2.3 Sample Collection and Analysis	37
3.2.3.1 Precipitation Samples	37
3.2.3.2 Litter Samples	38
3.2.3.3 Sulphation Discs	39
3.2.3.4 Soil Samples	40

TABLE OF CONTENTS

page

3.3 Jack Pine Stemflow Study 41

3.3.1 Experimental Design 41

3.3.2 Sample Collection and Analysis 42

3.4 Data Analysis 44

3.5 Terminology 45

4. DISTRIBUTION OF RAINFALL UNDER FOREST STANDS 47

4.1 Results 47

4.1.1 Precipitation 47

4.1.2 Throughfall 47

4.1.3 Stemflow 55

4.1.4 Net Rainfall and Interception 62

4.1.5 Sampling Intensity 64

4.2 Discussion 66

5. NUTRIENT TRANSFER FROM FOREST CANOPY TO SOIL 69

5.1 Results 69

5.1.1 Litter Production 69

5.1.2 Litter Nutrient Content 70

5.1.3 Nutrient Inputs in Precipitation 73

5.1.4 Addition of Nutrients to the Forest Floor ... 76

5.1.5 Nutrient Flux From Forest Vegetation to Forest Floor 81

5.1.6 Magnitude of the Chemical Components of Throughfall 83

TABLE OF CONTENTS

page

5.1.7 Seasonal Changes in Chemical Components of Throughfall 86

5.2 Discussion 87

6. IMPACT OF SULPHUR DIOXIDE ON THROUGHFALL AND STEMFLOW CHEMISTRY 93

6.1 Results 93

6.1.1 Acidity and Nutrient Content of Throughfall and Stemflow 93

6.1.2 Source of Nutrients in Throughfall and Stemflow 98

6.1.3 Determination of the Factors Influencing Throughfall Chemistry 107

6.1.4 Principal Component Analysis of Throughfall and Stemflow Data 109

6.1.4.1 Aspen Throughfall 110

6.1.4.2 Pine Throughfall 113

6.1.4.3 Aspen Stemflow 115

6.1.4.4 Pine Stemflow 117

6.1.5 Deposition of Sulphur in Throughfall and Stemflow 119

6.1.5.1 Trembling Aspen 119

6.1.5.2 Jack Pine 122

6.1.6 Effect of Sulphur Dioxide on Jack Pine

TABLE OF CONTENTS

page

Stemflow Chemistry 124

6.1.7 Effect of Sulphur Dioxide on Bark Leachate Acidity and Sulphur Content 126

6.2 Discussion 131

7. GENERAL DISCUSSION 139

8. CONCLUSIONS 143

9. LITERATURE CITED 149

10. APPENDIX 164

10.1 Soil Profile Descriptions 164

10.2 Characteristics of Representative Soil Samples ... 168

10.3 Acidity and Nutrient Content of Rain, and of Throughfall and Stemflow for Trembling Aspen, Jack Pine and Black Spruce. 171

10.4 Principal Component Analysis 178

10.5 Jack Pine Stemflow Experiment - Analysis of Variance 189

10.6 Comparison of the ratios of ions in rainwater and trembling aspen and jack pine throughfall. 192

10.7 Photographs of the six study plots used in the nutrient cycling study 1976 195

LIST OF TABLES

page

1. Description of the plots used for the nutrient cycling study 1976 31
2. Description of the four jack pine stemflow study sites 43
3. Amount of precipitation (mm) at the control site and the exposed site during the summer of 1976 48
4. Net rainfall, throughfall, stemflow and interception under a trembling aspen stand (control site) expressed as equivalent rainfall depth (mm) and percentage of gross rainfall 49
5. Net rainfall, throughfall, stemflow and interception under a trembling aspen stand (exposed site) expressed as equivalent rainfall depth (mm) and percentage of gross rainfall 50
6. Regression analysis of the relationships between throughfall (T), stemflow (S), per cent interception (I), and incident precipitation (P) ... 51
7. Net rainfall, throughfall, stemflow and interception under a jack pine stand (control site) expressed as equivalent rainfall depth (mm) and percentage of gross rainfall 53
8. Net rainfall, throughfall, stemflow and

LIST OF TABLES

page

interception under a jack pine stand (exposed site) expressed as equivalent rainfall depth (mm) and percentage of gross rainfall 56

9. Net rainfall, throughfall, stemflow and interception under a black spruce stand (control site) expressed as equivalent rainfall depth (mm) and percentage of gross rainfall 57

10. Net rainfall, throughfall, stemflow and interception under a black spruce stand (exposed site) expressed as equivalent rainfall depth (mm) and percentage of gross rainfall 58

11. The number of throughfall and stemflow gauges required to make the 95% confidence interval about the mean, equal to 10% of the mean 65

12. Nutrient content of tree litter expressed as per cent oven dry weight (ODW) 72

13. Comparison of the nutrient content of litter reported by various researchers 74

14. Nutrient content of precipitation at the control aspen site during the period 24 June to 2 October, 1976 75

15. Natural addition of nutrients to the forest floor of a jack pine ecosystem (control site) for the

period 23 July to 2 October, 1976 78

16. Natural addition of nutrients to the forest floor of jack pine, trembling aspen and black spruce ecosystems from the period 24 June to 2 October, 1976 79

17. The cycling of nutrients from forest canopy to the forest floor during the period 24 June to 2 October, 1976 82

18. Annual removal of nutrients from tree crowns by rain in this and comparable studies elsewhere in the world 85

19. Mean nutrient concentrations (ppm) and mean pH of incident rain collected during the summer of 1976 at the two sites of the nutrient cycling study 94

20. Mean total sulphation for the control site and the exposed site of the nutrient cycling study 94

21. Mean nutrient concentrations (ppm) and mean pH of throughfall and stemflow collected during the summer of 1976 95

22. Mean nutrient concentrations and pH of rain; and of trembling aspen and jack pine throughfall and stemflow 99

23. Increases in the ratio of ions relative to calcium due to the forest canopy of trembling aspen 102

24. Increases in the ratio of ions relative to calcium due to the forest canopy of jack pine 103

25. Cation and sulphate sulphur flux for trembling

aspen and jack pine for the control site and exposed sites of the nutrient cycling study, 1976. . 108

26. Deposition of sulphate sulphur in trembling aspen throughfall and stemflow for the control site and the exposed site from June through September, 1976 . 121

27. Deposition of sulphate sulphur in jack pine throughfall and stemflow for the control site and the exposed site from June through September, 1976 . 123

28. Acidity and sulphate sulphur content of jack pine stemflow sampled at four sites during June and July, 1977 125

29. Analysis of variance of pH, titratable acidity, sulphate sulphur and total sulphation between sites 125

30. Relationship between acidity and sulphate sulphur content of jack pine stemflow sampled at four sites during June and July 1977 128

31. The pH and sulphate sulphur content of washings from bark samples exposed to SO2 in a controlled environment chamber for seven days 130

32. Soil profile description - control aspen plot 165

33. Soil profile description - exposed aspen plot 165

34. Soil profile description - control jack pine plot .. 166

35. Soil profile description - exposed jack pine plot .. 166

36. Soil profile description - control spruce plot 167

37. Soil profile description - exposed spruce plot 167

38. Physical analyses of representative scil samples

from the nutrient cycling study plots 169
39. Chemical analyses of representative soil samples from the nutrient cycling study plots 170
40. Acidity and nutrient content of incident rain and trembling aspen throughfall and stemflow at the control site 172
41. Acidity and nutrient content of incident rain and trembling aspen throughfall and stemflow at the exposed site 173
42. Acidity and nutrient content of incident rain and jack pine throughfall and stemflow at the control site 174
43. Acidity and nutrient content of incident rain and jack pine throughfall and stemflow at the exposed site 175
44. Acidity and nutrient content of incident rain and black spruce throughfall and stemflow at the control site 176
45. Acidity and nutrient content of incident rain and black spruce throughfall and stemflow at the exposed site 177
46. Control aspen throughfall - principal component analysis 181
47. Exposed aspen throughfall - principal component analysis 182
48. Control pine throughfall - principal component analysis 183

49. Exposed pine throughfall - principal component analysis 184
50. Control aspen stemflow - principal component analysis 185
51. Exposed aspen stemflow - principal component analysis 186
52. Control pine stemflow - principal component analysis 187
53. Exposed pine stemflow - principal component analysis 188
54. One way analysis of variance of the pH of jack pine stemflow by site 190
55. One way analysis of variance of the titratable acidity of jack pine stemflow by site 190
56. One way analysis of variance of the SO4=-S concentrations of jack pine stemflow by site 191
57. One way analysis of variance of total sulphation (mg SO3 equivalent/cm²/day) by site 191
58. Increases in the ratio of ions relative to magnesium due to the forest canopy of trembling aspen 193
59. Increases in the ratio of ions relative to magnesium due to the forest canopy of jack pine 194

LIST OF FIGURES

page

1. Location of the study area showing the various plot locations in relation to the emission source .. 27
2. Layout of a typical plot used in the nutrient cycling study 35
3. Volume of stemflow per tree from trembling aspen for large storms (A) and small storms (B). 60
4. Incident precipitation and deposition of nutrients via throughfall in the three forest types (control site) from June through to October 1976 84
5. Components of the nutrient cycle for a forest ecosystem showing sites of nutrient accumulation and major pathways 90
6. Simplified Path diagrams showing the relationship between the principal components and variables for Aspen (Populus tremuloides Michx.) throughfall at a control site and a site exposed to sulphur dioxide 111
7. Simplified Path diagrams showing the relationship between the principal components and variables for pine (Pinus banksiana Lamb.) throughfall at a control site and a site exposed to sulphur dioxide . 114
8. Simplified Path diagrams showing the relationship between the principal components and variables for

Aspen (*Populus tremuloides* Michx.) stemflow at a control site and a site exposed to sulphur dioxide . 116

9. Simplified Path diagrams showing the relationship between the principal components and variables for pine (*Pinus banksiana* Lamb.) stemflow at a control site and a site exposed to sulphur dioxide 118

10. The variation in sulphate sulphur and acidity of jack pine (P. *banksiana* Lamb.) stemflow with increasing distance from a sulphur dioxide emission source 127

11. Simple model illustrating the relationship between atmospheric sulphur emissions and macroelement flux in two forest ecosystems 140

LIST OF PLATES

page

1. View of Great Canadian Oil Sands Ltd. extraction plant. 28
2. Control trembling aspen plot. 196
3. Exposed trembling aspen plot. 196
4. Control jack pine plot. 197
5. Exposed jack pine plot. 197
6. Control black spruce plot. 198
7. Exposed black spruce plot. 198

ABSTRACT

In the summers of 1976 and 1977 several field plots were established in northeastern Alberta to determine the distribution of rainfall under stands of trembling aspen (Populus tremuloides Michx.), jack pine (Pinus banksiana Lamb.) and black spruce (Picea mariana Mill.(B.S.P)). The relative amounts of Na, K, Ca, Mg and S returned to the soil, and recycled from trees to soil, in throughfall, stemflow and litterfall were determined for the three species. In addition, the effect of sulphur emissions from an oil sands extraction plant on nutrient return in throughfall and stemflow was investigated.

The amount of net precipitation (expressed as a percentage of incident rain) reaching the forest floor under trembling aspen, jack pine and black spruce was 91%, 85% and 76% respectively. Throughfall averaged about 84-85% of incident precipitation for both trembling aspen and jack pine and about 76% for black spruce. Stemflow averaged 7-8% of incident precipitation in trembling aspen, about 0.2-0.4% in jack pine, and less than 0.1% in black spruce.

The jack pine forest floor recieved a total of 8 kg/ha of Ca, 7 kg/ha of Mg, 3 kg/ha of K, 2 kg/ha of S and 1 kg/ha of Na over the summer period. The trembling aspen forest floor received 44 kg/ha of Ca, 30 kg/ha of Mg, 13 kg/ha of K, 4 kg/ha of S and 1 kg/ha of Na. Corresponding values for black spruce were 9 kg/ha of Ca, 6 kg/ha of Mg, 4 kg/ha of K

and 0.4 kg/ha of Na. For all three species litterfall was the most important means of addition of Ca and Mg to the forest floor (53-91% of the total depending on the species) over the summer period. Trembling aspen litterfall supplied about 50% of the Na and 71% of the K to the forest floor. Throughfall added most of the K for both jack pine and black spruce (70%), about twice that added in litterfall. The trembling aspen canopy absorbed sodium from incident rain resulting in low amounts in throughfall and stemflow. Almost all the sodium reaching the forest floor in jack pine and black spruce was via throughfall, and was largely derived from incident precipitation. Stemflow added little (1-4% of the total) nutrients to the soil.

The acidity of rain decreased as it passed through the canopy of trembling aspen whereas rainfall acidity increased as it passed through the canopy of jack pine. The acidity of jack pine throughfall and stemflow increased at sites exposed to sulphur dioxide as compared to control sites. Throughfall decreased in pH by about 0.3 units and stemflow decreased by about 0.8 to 1.1 pH units. The amounts of sulphur deposited in net precipitation (throughfall plus stemflow) beneath trembling aspen and jack pine was greater at sites close to the emission source as compared to remote control sites. The hydrogen ion concentrations in jack pine throughfall and stemflow were highly correlated with sulphate sulphur concentrations at sites close to the emission source but poorly correlated at the control sites.

For both jack pine and trembling aspen, larger quantities of the cations K^+, Ca^{++} and Mg^{++} were removed from the canopies at the site exposed to sulphur dioxide compared to the control sites.

1. INTRODUCTON

In the past few decades serious environmental problems have become apparent with increasing emissions of atmospheric sulphur dioxide (Anon 1972). On a global scale anthropogenic emissions of sulphur compounds are estimated to be 70 x 10^6 tons S/year (Eriksson 1963, Kellogg *et al.* 1972) with approximately an equivalent amount arising from natural emissions. Canada has about 5 per cent of the world total anthropogenic emissions (Katz 1977) while 0.23 million tonnes per year (or approximately 0.4 per cent of the world total) are emitted in Alberta (Tollefsen 1972).

The main sources of anthropogenic sulphur in Canada are the smelting of sulphide ores and fossil fuel combustion (Summers and Whelpdale 1976). In Alberta, the main source of sulphur oxides is the processing of natural gas (Summers and Whelpdale 1976). Sulphur dioxide is a primary air pollutant as well as a primary toxicant. Low doses of sulphur dioxide may be harmless or even beneficial since sulphur is an essential plant nutrient. However, an increased uptake of sulphur dioxide by vegetation may cause more and more changes in the system, first reversible, later irreversible, until breakdown of the system occurs (Knabe 1976). The effect of sulphur dioxide on ecosystems has frequently been described in terms of zoned patterns of environmental stress around a point source (Gordon and Gorham 1963).

Sulphur dioxide may be oxidized and hydrolyzed by a

series of complex atmospheric reactions to form sulphuric acid which may cause precipitation to be acidic (Brosset 1973). A trend towards increased acidity of precipitation has been found in the heavily industrialized regions of the world, namely northwestern Europe and the northeastern United States.

Distilled water in equilibrium with atmospheric carbon dioxide has a pH of 5.7 since carbon dioxide combines with water to form carbonic acid. This pH value may be regarded as the neutral point for rainwater (Barrett and Brodin 1955). In some parts of Scandinavia acidity of rain has increased by more than 200 fold since 1956 (Oden 1968) with pH values as low as 2.8 being recorded (Likens et al. 1972). Currently the pH of precipitation in much of the northwestern United States averages annually between 4.0 and 4.2 and for southwestern Norway below 4.3 (Overrein 1977). Slightly acid precipitation has been reported in regions downwind of gas processing plants in central Alberta (Walker 1969, Summers and Hitchon 1973).

Recent laboratory experiments have demonstrated that increased acidity of artificial rain and mists can increase the leaching of inorganic and organic compounds from foliage (Wood and Bormann 1975), accelerate cuticular erosion of leaves (Shriner 1976), and produce leaf damage when the pH values fall below 3.5 (Wood and Bormann 1975). These results suggest that acid precipitation may be accelerating foliar

leaching of nutrients from exposed forest trees.

Odum (1971) has stated:

"The rates of exchange or transfers from one place to another are more important in determining the structure and function of an ecosystem than the amounts present at any one time in any one place. To understand and thereby control man's role in the cycles of materials, cycling rates as well as standing states must be quantitated."[1]

In addition, intrasystem nutrient cycling mechanisms in forests constitute a nutrient conserving system in which the major transfer processes are critical for the system to be maintained. If acid rain is increasing the rate of transfer of nutrients from forest to soil then it is affecting the entire nutrient cycling mechanism of affected forest ecosystems. Such a disruption could lead to a reduction in forest productivity. Indeed reduction in forest production by acidity of rain has been suggested (Engstrom et al. 1971).

Because of the complexity of forest ecosystems, it is not always possible to extrapolate laboratory results to field conditions. The few field investigations to date on the influence of sulphur emissions on nutrient cycling have not used a control area with which to compare foliar leaching data from polluted areas (eg. Cole and Johnson 1977, McColl and Bush 1978). This study was therefore

---

1 Odum, E.P., 1971. Fundamentals of Ecology 3rd Ed. W.B. Saunders Co. pg 93.

initiated to obtain accurate field information on the influence of sulphur emissions on the return phase of nutrient cycling of three boreal forest ecosystems. The sites were located in an area of northern Alberta where there was only a single emission source. This enabled data from plots distant from the emission source (> 100 km) to be compared to plots located in the vicinity of the emission source. In addition, there is limited information on nutrient cycling in boreal forest ecosystems (Foster and Morrison 1976). As forest management practices become more intensive in Canada the need for studying nutrient cycling and site fertility will increase. Such information is particularly important in enabling efficient use of fertilizers. The objectives of this investigation were therefore:

1 To compare the chemical composition of throughfall, stemflow and litterfall of trembling aspen (Populus tremuloides Michx.), jack pine (Pinus banksiana Lamb.) and black spruce (Picea mariana (Mill.) B.S.P.). This would provide information on the amounts of nutrients returned to the soil and the amounts of nutrients recycled from vegetation to soil in throughfall, stemflow and litterfall.

2 To determine whether sulphur emissions are causing an increase in the foliar leaching rates of these same

species and to evaluate differences, if any, of this effect between species.

2. LITERATURE REVIEW

2.1 NUTRIENT INPUTS

Atmospheric deposition has received increasing attention as an input to nutrient budgets of ecosystems (Ingham 1950, Junge and Werby 1958, and Tamm 1959). In coastal areas, windblown salt aerosols are a significant input to mineral cycles (Clayton 1972). Etherington(1967) concluded that salt spray provided an adequate supply of micronutrients for several plant associations on sandy, nutrient deficient soils in Wales.

Aerosols may also be of terrestrial origin. Smith et al. (1970) provided extensive data on dust deposition in the U.S. in relation to geography, climate and cultivation pattern. Winkler(1970) stated that terrestrial dust makes up the bulk of atmospheric dust and may reflect the soil composition of areas up to 150 miles away. Local effects of dustfall from an unpaved road may also be an important source of nutrients for forest ecosystems (Tamm and Troedsson 1955). Aerosols may also be derived from industrial processes such as the burning of fossil fuels (Dovland et al. 1976). These aerosols may settle on the vegetation and be subsequently washed off by rain (Brosset 1976). This process, therefore, represents an addition of nutrients to the soil through the existence of the plant as a physical structure.

Atmospheric aerosols may act as condensation nuclei and be removed from the atmosphere by falling raindrops (Junge and Gustafson 1957). Winkler (1976) has stated that dust from glacial till found on construction sites and flood plains is quite reactive with acids in precipitation despite its brief contact between the cloud base and the surface of the terrain. Sumi et al. (1959) described gypsum as the chief water soluble component of the atmosphere of almost all industrialized areas and this may explain the frequent high calcium content of the rain in these regions. Indeed, Barret and Brodin (1955) implicated a large cement factory in southwest Sweden as the cause of an unusually high pH and calcium content of precipitation in that region. Dust has been used to explain in part regional and seasonal variations in the nutrient content of rainwater (Winkler 1976).

A low but not negligible amount of nutrients may be added to the soil in rainwater. Madgwick and Ovington (1959) showed that the amounts of sodium, potassium, calcium, and magnesium contained in precipitation was equivalent to or greater than the permanent annual incorporation of nutrients in the thirteen different forests they analysed. Paivenen (1974) calculated that gross rainfall would replace the amounts of potassium, phosphorus and nitrogen removed by harvesting scots pine (Pinus sylvestris) in 6.3, 13.7 and 9.5 years respectively.

The chemical composition of rainwater has been reviewed by Eriksson (1952) and Junge and Werby (1958). The concentration of most ions in rain generally decreases as the duration of a particular shower increases, indicating the presence of a limited quantity of ions in the lower atmosphere at a given time (Tamm 1959, Attiwill 1966). For long periods of rainfall sampling, however, variation in the quantity of ions in the lower atmosphere during each period may decrease. Since total accession of an ion per unit area is the product of concentration of the ion and the amount of rain per unit area, the total accession must increase as the amount of rain during a given period increases (rainfall intensity). The relationship of concentration of ions in rain to rainfall intensity must therefore be curvilinear (Madgwick and Ovington 1954, Attiwill 1966).

The chemistry of precipitation varies greatly from area to area depending on the origin of air masses. Ratios of ionic concentrations in rainwater have been shown to be related to the origin of the air masses (Eriksson 1952). Generally it has been assumed that sea spray particles serve as the principal nuclei for water vapour condensations (Junge and Gustafsen 1957). Therefore, the ratios of the concentrations of sodium, the most abundant ion in sea water, to the concentrations of the other ions have frequently been used to interpret the geographical distribution of ions in rainwater (Carlilse et al. 1966). In Australia, Hutton and Leslie (1958) showed that sodium:

potassium and sodium: calcium ratios decreased from values approaching those in sea water with increasing distance from the ocean and in some inland sites calcium became the dominant cation. Calcium was reported as the dominant cation for rain in Utah (Hart and Parent 1974), northern Minnesota (Comerford and White 1976) and at Hubbard Brook, New Hampshire (Eaton et al., 1973). This reflects the continental origin of air masses affecting these regions. The calcium: magnesium ratio is often used as an indication of air-borne chemicals (Eriksson, 1952). Precipitation from air masses directly off the ocean generally has a calcium: magnesium ratio approaching that of sea water whereas continental precipitation generally has a much higher ratio. (Eaton et al. 1973)

2.2 DISTRIBUTION OF PRECIPITATION UNDER FOREST STANDS

The nutrient cycle is strongly coupled with the hydrologic cycle so it is necessary to investigate the latter when studying the former. The distribution of rainfall under a forest canopy is affected by tree species, size and form of the tree and meteorological factors such as storm size and intensity and wind velocity (Ovington 1954, Voigt 1960, Geiger 1965). The earlier literature has been summarized by Kittredge (1948), and Zinke (1967). Helvey and Patric (1965) provided a summary of investigations carried out in the U.S.

Voigt (1960) investigated the distribution of water beneath red pine (Pinus resinosa), eastern hemlock (Tsuga canadensis) and American beech (Fagus grandifolia). He showed stemflow was a particularly important component of the water budget of forest stands and that differences between tree species were related to bark texture. Stemflow volume was shown to bear a linear relationship with the square of dbh in a Scots pine stand (Rutter 1963) and for a given-sized storm, stemflow volume increased with the basal area. A similar relationship was shown by Pressland (1973). Pressland also showed that stemflow and interception were positively correlated with precipitation while negative relationships were found between tree size and throughfall and stemflow for various classes of precipitation events. Kittredge et al. (1941) found that stemflow was not apparently related to crown-length density, tree height, basal area or crown area, but tended to increase with excess or deficit of tree height as compared with adjacent trees.

Jackson and Aldridge (1973) found that throughfall, stemflow, net rainfall, and interception loss were each highly correlated with gross rainfall for two stands of Kamahi (Weinmannia racemosa) in New Zealand. Orr (1972) also found that gross precipitation was the primary controlling variable in both throughfall and stemflow. He found however that canopy density did account for a portion of the throughfall variation and similarly dbh for stemflow. A combination of these two relationships yielded an equation

for net rainfall. Clements (1970) found the relationship of stemflow to gross rainfall for largetooth aspen (Populus grandidentata) was closely related to that developed by White and Carlilse (1968) for some other hardwood species, and his throughfall equation was in very good agreement to that developed by Helvey and Patric (1965) from 12 combined throughfall equations for various hardwood species.

The amount of precipitation intercepted by forest canopies has been investigated by various researchers (Kittredge et al. 1941, Orr 1972, Jackson and Aldridge 1973, Szabo 1975). Zinke (1967) recorded 0.25-9.15 mm interception storage capacity values with conifers having higher values than deciduous species, in general. The statistical aspects of throughfall and stemflow sampling have been the subjects of papers by Reynolds and Leyton (1963) and Kimmins (1970).

2.3 LEACHING OF NUTRIENTS FROM TREE CROWNS

As early as 1805, De Saussure noted that water in contact with leaves contained alkaline salts. Wehmer (1892) noted that when plants were subjected to rain, substances were given off from the plants. Le Clerc and Brazeale (1908) performed experiments that showed living plants lost part of their salts when washed with rain. Similar experiments performed by Guilbert, Mead and Jackson (1931), Mes (1954) and Dalbro (1957) demonstrated that rainfall may remove considerable quantities of nutrient elements from the

foliage of horticultural plants. Dew was also found to remove salts from plants. Phyllis and Mason (1942). showed that dew collected from cotton plants contained potassium and calcium.

Similarly, studies of the elemental content of precipitation under forest stands (Tamm 1951, Madgwick and Ovington 1959, Will 1959, Voigt 1960) demonstrated that rainwater which has passed through tree crowns contains higher quantities of nutrient elements than incident rainfall.

A number of researchers has recognized the possibility that aeorsols and dust may adhere to the leaves, branches and stems and may be subsequently washed off in the rain and hence contribute to the chemical composition of throughfall and stemflow (Eriksson 1955, Carlilse et al. 1967, Duvigneaud and Denaeyer-DeSmet 1964). Hart and Parent 1974 suggested that dry fallout of dust in some rain free periods was responsible for high nutrient values of throughfall under Douglas fir (Pseudotsuga menziesii var. glauca) and Rocky Mountain Juniper (Juniperus scopulorum) in northern Utah. Nihlgard (1970) suggested that some of the magnesium, sodium, calcium and chloride in throughfall could have been derived from aerosols while potassium and manganese must have been derived from leaching in beech (Fagus sylvatica) and spruce (Picea abies) forests in Sweden. It has been suggested (Henderson et al. 1977) that differences in net

removal among different forest types may reflect differential trapping of particulates and aerosols by various tree species. Attiwill (1966) demonstrated that the alteration of the chemical composition of rainwater by a Eucalyptus forest was largely due to foliar leaching. Leaching has been shown to be widespread in nature and nutrients have been leached from all of the 140 species so far investigated (Tukey et al. 1965). Minerals leached from foliage include both major and minor inorganic minerals as well as carbohydrates, amino acids and at least fifteen organic acids (Mecklenburg et al. 1966).

The amounts of elements leached from tropical trees are greater than for forests in temperate regions and represent a greater propcrtion of the mineral flux (Rodin and Brazilevich 1967). This is probably due to the high rainfall and the fact that tropical trees are evergreen and have a high leaf area index (Bernhard-Reversat 1975).

The degree to which nutrients are leached from tree crowns is also dependent on the tree species (Madgwick and Ovington 1959, Eaton et al. 1973, Henderson et al. 1977). Similar differences were noted by Tukey et al. (1958) in various vegetable crops. These differences are dependent on the nutrient being considered. For example, Henderson et al. (1977) observed no differences in the nitrogen and phosphorus contents of throughfall of four forest types presumably because these elements are primarily present in

organically bound form and are less available for leaching. Differences in nutrient content of throughfall between species can only be partially explained by foliar concentration differences. (Eaton et al. 1973, Henderson et al. 1977)

In general, deciduous trees lose more nutrients than conifers during the growing season but in the winter the reverse is true (Madgwick and Ovington 1959, Henderson et al. 1977). On the other hand, Nihlgard (1970) found that despite 20 percent less throughfall under spruce, the amounts of nutrients in spruce throughfall were two to three times greater than for beech over the summer. On an annual basis the quantities of potassium, calcium and magnesium were greater for a mixed hardwood stand than for a natural loblolly pine stand (Wells et al. 1972).

A number of researchers has noted a seasonal variation in the quantities of nutrients removed from the forest canopy by precipitation (Abee and Lavender 1972, Will 1959). Denaeyer-DeSmet (1966) found that beech (Fagus sylvatica) leaves lost much higher levels of potassium after they had become coloured in the fall. Eaton et al. (1973) found that calcium and magnesium concentrations were relatively constant during the summer, then reached their maximum just prior to leaf senescence. Potassium and chloride reached their maxima after leaf senescence. High throughfall concentrations of magnesium and calcium after senescence

were also noted by Reiners (1972) for *Quercus ellipsoidallis*, *Thuja occidentalis*, *Fraxinus nigra*, *Acer rubrum*, and *Ulmus americana*, and by Miller (1963) for mountain beech (*Nothofagus truncata*).

Foster (1974) found that leaf wash was the most important source of potassium additions to the soil in a jack pine stand in Ontario. The quantities of nitrogen, phosphorus, calcium and magnesium in throughfall were lower than potassium and were derived primarily from precipitation entering the ecosystem. Greater quantities of potassium in throughfall than in litterfall have also been reported in Douglas-fir (*Pseudotsuga menziesii*) (Cole *et al.* 1967), radiata pine (*Pinus radiata*) (Will 1959), and Pacific silver fir (*Abies amabilis*) (Turner and Singer 1976). Greater amounts of potassium and magnesium in throughfall than in litterfall were reported in Douglas-fir (Abee and Lavender 1972) and sessile oak (*Quercus petraea*) (Carlilse *et al.* 1967).

Tukey *et al.* (1958) found that the relative leachability of radioisotopes from the leaves of young squash and bean plants was Na>Mn>Cu>Mg>S>K>Cl. Potassium which was leached at a moderate rate from young leaves was the most readily leached nutrient from mature leaves. Zamierowski and McCloskey (1975) also found that potassium was the only element lost by both young and mature leaves of the three tree species (*Podocarpus gracilior*, *Podocarpus*

milaniranus and Olea africana) they investigated. Losses of magnesium and manganese were greater for young leaves of all species. Attiwill (1966) found the order of leaching from the canopy of Eucalyptus (Eucalyptus obliqua) forests to be Na>K>Ca>Mg while Miller (1963) found the order from mountain beech in New Zealand to be Cl>Na>K>Ca>Mg. This is consistent with the pattern of enrichment of throughfall and stemflow with bases of K>Ca>Mg reported by many authors (Tamm 1951, Madgwick and Ovington 1959, Carlilse et al. 1967, Foster 1974, Henderson et al. 1977). However Eaton et al. (1973) found the order of importance of leaching to be Na>S>K>Mg>Ca>N>P for a hardwood canopy at Hubbard Brook while Gosz et al. (1975) reported that sodium was very difficult to leach from detached leaves of northern hardwood species. Nihlgard (1970) found the ratio between nutrient concentrations in throughfall plus stemflow and nutrient concentrations in incident rainfall for beech (F. Sylvatica) forest was Mn>>K>>Mg>Cl>Ca>Na>S>P>N and the corresponding ratio for spruce (P. abies) forest was Mn>>K>>P>S>Mg>Ca>Cl>Na>N. In general, the order of leaching of bases from trees appears to be K>Ca>Mg but there are numerous exceptions to this order.

2.3.1 Nature of the Leaching Process

Stenlid (1958) in his survey of many leading experiments with individual (often detached) leaves concluded that potassium is leached more readily than other

cations. Carlisle et al. (1967) noted that the less mobile bivalent calcium and magnesium were removed in smaller quantities than the more mobile monovalent bases (potassium and sodium). Potassium which occurs in an inorganic form in the plant, can be readily removed by water, whereas calcium which occurs as insoluble pectates in the cell wall, and magnesium, which is a mobile element in the plant and a constituent of chlorophyll, are leached to a lesser degree (Foster 1974). Tukey et al. (1958) showed that mineral nutrient-deficient or otherwise unhealthy plants were more susceptible to leaching than were healthy plants. It appears that the physiological status of the element in the leaf and the physical condition of the leaf are factors in determining the rate of removal of an element by leaching.

Lausberg (1935) found that over extended periods of leaching, losses could amount to several times the amount of nutrients found in the leaf. D'Souza (1974) also found a greater loss of ^{45}Ca, ^{89}Sr and ^{226}Ru from leaves of intact plants than from excised leaves. Tukey et al. (1958) demonstrated that as nutrients are leached from the leaves they are replaced by translocation from the stems and roots. Mecklenberg and Tukey (1964) showed that the rate of root uptake and translocation of ^{45}Ca to bean stems and foliage was greater per gram dry weight in plants which were leached than in plants which were not leached. Up to 40 per cent of the ^{45}Ca absorbed and translocated during the leaching period was leached from the foliage. They suggested that the

pathway of calcium translocation and the foliar leaching of calcium were closely related.

Mecklenberg et al. (1966) showed that plant energy level had little influence on leaching losses of ^{45}Ca and ^{87}Rb, supporting the hypothesis that leaching is primarily a passive process. They also showed that the most recently absorbed ^{45}Ca was the most easily leached suggesting that the calcium that is translocated within the plant is the major source of leached calcium.

To determine the exact source of the leached calcium they measured the specific activity of ^{45}Ca (ratio of ^{45}Ca to total calcium) in various calcium fractions within the plant and computed the change in specific activity of the leachate over time with the change in specific activity of the fractions. They found that the entire exchangeable calcium pool of the plant is the primary source of leached calcium, and very little if any leached calcium is derived from within the cells themselves or from nonexchangeable forms of calcium. Similarily D'Souza (1974) indicated that calcium ions leached from bean leaves were largely derived from the exchangeable fraction.

On the basis of these results Mecklenberg et al. (1966) proposed the following hypothesis to explain the foliar leaching of calcium:

"Cations such as calcium may be swept upward in the transpiration stream in the stem to the leaves, involving in part exchange reactions in this process. The subsequent

distribution of calcium within the leaf and movement through the cuticle is also an exchange phenomenon involving exchange sites on the cell walls and on the pectinaceous materials which penetrate the cuticle."[1]

This is substantiated by the work of Yamada et al. (1964) who emphasized the importance of cations in the movement of ions through the cuticle. Keppel (1967) has demonstrated the ion exchange capacity of the leaf cuticle of potato, sugar beet and barley seedlings. The exchange activity of the ions was found to be dependent on their hydration and valency. Differences in plant habit, spacial orientation of the leaves, and their morphological state and ability to retain drops of fog, rain and dew did not influence the exchange capacity.

Calcium is leached from the leaf by either exchange of calcium on the cuticle and cell wall exchange sites by hydrogen from the leaching solutions, by diffusion of ions from the translocation stream within the foliage into the leaching solution, or by a combination of both exchange and diffusion (Mecklenberg et al. 1966). This hypothesis is also applicable to other cations such as potassium, rubidium and strontium. The leaching of ^{32}P and ^{35}S, however, were not affected by experimental treatments to the same degree as cations suggesting that a different mechanism of leaching is involved for these nutrients (Tukey et al. 1965).

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[1] Mecklenburg, R.A., Tukey, A.B. Jr., and Morgan J.V. 1966. A mechanism for the leaching of calcium from foliage. Plant Physiol. 41. pg. 613.

It is important to note that Franke (1964) demonstrated the presence of regular systems of pathways in the outer cells of the epidermis (ectodesmata) which may also function in the exchange of material between the interior and exterior of the leaf. Guttation (secretion of salts) from plant hydathodes has been noted as the cause of heavy salt deposits on the leaves of cauliflower (Tukey and Morgan 1962) and recently fertilized lawn grass (Curtis 1944). This process is most commonly associated with halophytic plants (Stenlid 1958).

On the basis of the exchange hypothesis, the volume of leaching solutions need only be sufficient to wet the leaf surface. Any additional volume would increase the exchange only slightly. This substantiates reports by Attiwill (1966) and Tamm (1958) that the efficiency of leaching is greatest during the first hours after wetting and that efficiency of leaching is greater for dew and light rain of long duration than for heavy rains of short duration. Also during rain the film of water on the leaf surface in constantly renewed. Uptake of nutrients by the leaves could not occur if the substances were not adsorbed in the short time of contact with the leaf (Keppel 1967). The hypothesis of cation exchange is also consistent with the observation that considerable quantities of radionuclides are taken up by plants through the leaf surface (D'Souza 1974) and the well known fact that plants may be efficiently fed with necessary

elements by spraying with dilute solutions (Boynton 1954, Tiffin 1972).

As the ion-exchange reactions which take place on the leaf surface need the presence of water, the ions concerned with these processes are hydrated. The cations can therefore be arranged in order of the exchange strengths which is dependent on the ratio of the charge to hydrated ionic radius (Keppel 1967). Such a series is known as a lyotropic or Hofmeiser series (Blasius 1958). Keppel (1967) showed for sugar beet foliage the order; H>Ca>Cs>K>Na suggesting that hydrogen ions are bound the strongest. This explains his observation that the adsorption of Cs in acid solution was reduced to a third from the exchange of Cs in neutral solution. Mecklenberg et al. (1966) proposed that water on the leaf surface dissolves CO2 from the air to form carbonic acid. The carbonic acid dissociates and the released hydrogen exchanges with cations on the cuticle exhange sites to form alkaline carbonates, which either remain in the leaching solution or are precipitated onto the leaf surface. This explains the observations of whitish accumulations of carbonates on the leaves of chrysanthemums growing in the greenhouse (Morgan 1963) and the alkaline nature of leachates noted by Arens (1934). This also substantiates the conclusion of Greendale and Nye (1964) that bicarbonate was the primary anion in leachate from tropical trees. Cole and Johnson (1977) also observed that bicarbonate was the predominant anion in throughfall from a Douglas-fir

ecosystem.

Tukey et al. (1965) found that a greater amount of ^{45}Ca was leached from bean leaves in solutions of 0.1 M KH_2PO_4 than in 0.01 M KH_2PO_4 or distilled water. The increased concentration of hydrogen ions in the KH_2PO_4 solutions therefore increased the rate of exchange of calcium. Fairfax and Lepp (1975) showed that an increase in the acidity of the leaching solution resulted in a significant ($p<0.01$) increase in the leaching of calcium from tobacco leaves. There was, however, an increased retention of potassium which they could not explain. Wood and Bormann (1974) showed that increased acidity of an artificial mist caused an increase in the leaching of calcium, potassium and magnesium in pinto bean (*Phaseolus vulgaris var. pinto*) and sugar maple (*Acer saccharum*). The nature of the leaching solution is therefore an important factor in the loss of cations and Mecklenberg (1964) found that cations in the leaching solution influence leaching of calcium in relation to their rate of replacement of calcium on the exchange sites. Keppel (1967) found that the exchange of cations by leaves was not only dependent on the type of cation in the exchange solution but also on its concentration.

Tukey et al. (1958) showed that although very young leaves appear delicate and fragile they are less susceptible to leaching losses than older leaves. Leaching losses were greatest when leaves approached senescence. Tukey et al

(1966) suggested that young, vigorously growing tissues accumulate calcium from exchange sites, thus reducing the amount of exchangeable calcium available for leaching. In addition, calcium is accumulated within the cells and is incorporated into calcium pectates of cell walls where it is not subject to leaching. In mature tissues, there is a reduced rate of cellular accumulation (due to slower growth) leaving more exchangeable cations for foliar leaching. However, if the leaves are damaged, nutrients may be leached easily, from both young and mature tissues (Tukey et al. 1958). Stenlid (1958) suggested that this may be due to increased permeability of the cytoplasm. According to Barinov and Ratner (1959) there is a time lag of several hours between the sorption of a substance on the leaf surface and evidence of it in the interior of the leaf. This time lag is directly related to the thickness of the cuticle. Zamierowski and McCloskey (1975) noted that the youngest leaves of trees used in their leaching experiments had a distinctly more hydrophobic cuticle. The leaves became more hydrophilic with maturity and especially during senescence. They suggested that this fact, plus the greater cracking of the cuticle with age, could explain the greater leaching losses associated with senescent leaves.

Thomas (1969) found more leaching of ^{45}Ca from yellow senescent leaves than from green leaves and presumed this to result from increased leaf permeability due to breakdown of the cuticle. Fogg (1947) noted that changes in

susceptibility to leaching were related to the wetting properties of the leaf. Stenlid (1958) stated that salts are lost more rapidly from leaves at high than at low temperatures and that the wetability of leaves increases with temperature. This is perhaps related to the influence of temperature on cuticular development (Skoss 1955) or due to increased evapo-transpiration (Eaton et al. 1973).

2.4 NUTRIENT CONTENT OF LITTER

A large number of researchers have investigated the amounts of nutrients in litter of different tree species. Alway and Zon (1930) summarized early investigations in central Europe and the U.S. and other reviews have been prepared by Blow (1955), Tarrant et al. (1951) and Scot (1955). More recently Bray and Gorham (1964) published a very comprehensive review of litter production in forests of the world. There is, however, a paucity of information on the litter production of boreal forest tree species, particularly for black spruce (Picea mariana), trembling aspen (Populus tremuloides) and jack pine (Pinus banksiana) and to my knowledge no such information is available for western Canada. Alway and Zon (1930) determined the nitrogen, calcium, phosphorus, potassium and sulphur content of jack pine litter at two sites in northern Minnesota. The macroelement content of jack pine litterfall was reported by Foster (1974) and Foster and Gessel (1972) for sites in northern Ontario. Coldwell and Delong (1950) investigated

the nutrient content of trembling aspen litter at Montreal while Remezov and Bykova (1953) and Sviridova (1960a) reported the nutrient content of litter from aspen (Populus tremula) stands at Voronezh, USSR. Bray and Dudkiewicz (1963) determined the standing crop of leaves on an annual basis for two aspen stands; one at Itasca, Minnesota and the other at Dorset, Ontario. Recently Van Cleve and Noonan (1975) reported data for trembling aspen and paper birch (Betula papyrifera) stands at Fairbanks, Alaska.

Black spruce litterfall has been reported as part of a fertilization and thinning study in northern Quebec (Weetman and Hartland (1963) and Mahendrappa and Ogden (1973) determined the nitrogen content of black spruce litter in central New Brunswick.

3. MATERIALS AND METHODS

3.1 Description of the Study Area.

The study area was located in the Fort McMurray region of northeastern Alberta between 56°-57° N and 111°-112° W (Figure 1). It is part of the mixedwood section (B 18a) of the boreal forest region (Rowe 1972). The growing season, based on a 5°C index (42°F), lasts from the end of April to early October, an average of 165 days. The average annual precipitation is 432 mm with 280 mm falling during the period from May to September.

The only sources of sulphur emissions in the study area were located at the Great Canadian Oil Sands Ltd. processing plant located at Tar Island about 70 km north of the town of Fort McMurray (Figure 1 and Plate 1). At this plant there are two main sources of sulphur emissions. The power house stack is estimated to emit an average of 120 tonnes S/day and the incinerator stack about 15 tonnes S/day. In addition there are two flares which are intermittant sources of smaller amounts of sulphur oxides (M. Strosher pers. comm. 1978).[1]

3.2 NUTRIENT CYCLING STUDY

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[1] M. Strosher. Project manager, Pollution Control Division, Alberta Environment.

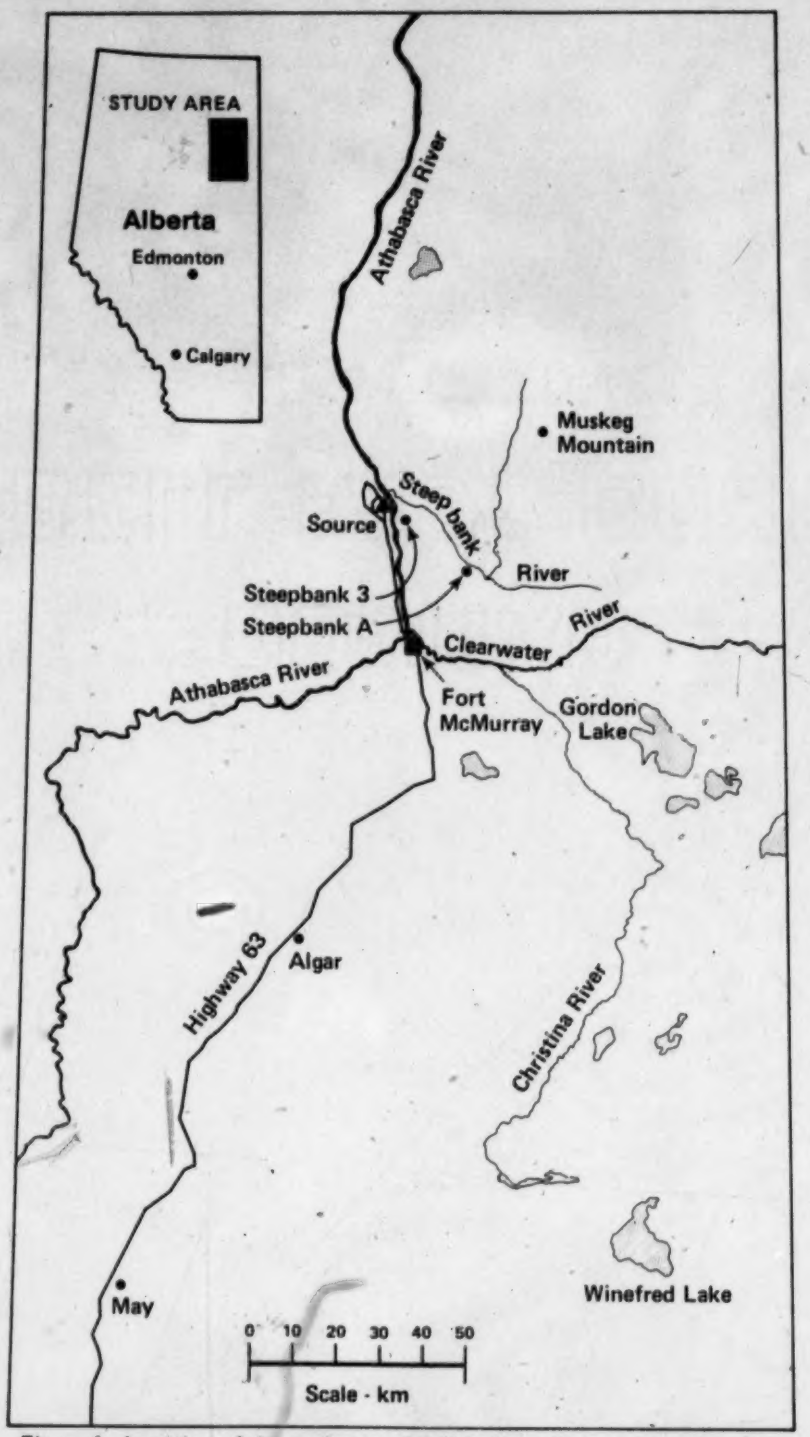

Figure 1 Location of the study area showing the various plot locations in relation to the emission source ▲. Nutrient cycling study plots were located at Steepbank A (exposed site) and Algar (control site). Jack pine stemflow plots were located at Steepbank 3, Muskeg Mountain, Algar, and May.

Plate 1. View of Great Canadian Oil Sands Ltd. extraction plant. The Athabasca River is on the right. Note the power house stack and the flare stack.

The tree species studied were trembling aspen (*Populus tremuloides* Michx.), jack pine (*Pinus banksiana* Lamb.) and black spruce (*Picea mariana* (Mill.) B.S.P.). It should be noted that in the study area there is some hybridization between jack pine and lodgepole pine (*Pinus contorta* Dougl. *Var. latifolia*. Engelm.). Branch and cone samples from the jack pine sites used in this study were examined in the laboratory and it was concluded that the variability within sites was no greater than the variability between individual jack pine trees. The jack pine trees at each site exhibited predominantly jack pine characteristics.

The three species were chosen because they are the predominant tree species in the region and because they represent three very different types with regard to tree form, bark texture and site preferences. They also differ in sensitivity to sulphur dioxide with trembling aspen being regarded as the most sensitive of the three species (Linzon 1972, Loman *et al.* 1972). Jack pine is regarded as being intermediate in sensitivity and black spruce as the least sensitive (S.S. Malhotra pers. comm. 1978).

3.2.1 Experimental Design

Two study sites were chosen. The control site was in an

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1 S.S. Malhotra. Research scientist, Northern Forest Research Centre, Canadian Forest Service, Environment Canada, Edmonton

area free from SO2 pollution. It was located about 100 km SSW of the emission source (Figure 1.), at an elevation of 781 m. Average precipitation from May to September (eight year mean) recorded at the nearest forestry weather station (Algar) is 394 mm with the greatest amount occurring during July. The exposed site was in an area subject to SO2 pollution. It was located about 32 km SE of the emission source at an elevation of approximately 500 m. (Figure 1). The average (seven year mean) precipitation from May to September at the Gordon Lake weather station (488 m) was 323 mm. The greatest amount of precipitation occurred during July.

Three plots were established at both the control and exposed sites, one for each species. It was not possible to have two plots for each species at both control and exposed sites. Difficulty in locating similar stands, lack of time to establish these plots at the beginning of this study, and the prohibitive number of sample collectors that would be required precluded this more desirable experimental design. Each plot consisted of a nearly pure stand of each tree species. A description of the study plots is given in Table 1. For jack pine and trembling aspen the control and exposed plots had similar tree heights and stand densities. The difference in the diameters of trees selected for stemflow gauges was significant but barely so (Student's t-test) for trembling aspen ($p<0.05$) and not significant for jack pine ($p>0.05$). The spruce plots were quite different in stand

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density, tree heights and stem diameters. At both sites, plots were chosen to be as close together as possible. This minimized topographic differences and ensured each plot received similar amounts of precipitation. This also ensured that the exposed plots received similar levels of sulphur dioxide emissions. Detailed descriptions of the soils at each plot are given in Appendices 10.1 and 10.2. Photographs of each plot are found in Appendix 10.7.

The black spruce and trembling aspen control plots were located about 1 km west of the forestry weather station (Algar) and were about 50 m apart. The black spruce plot was located on poorly drained glacial till. The dominant tree species was mainly black spruce with some individual jack pine trees scattered throughout the plot. Several of these jack pine trees were dead. The shrub stratum consisted primarily of Ledum groenlandicum. The forest floor was covered by a continuous carpet of feather and turf mosses (Polytrichum, Ptilium, and Hylocomium spp.).

The control aspen plot was located on well-drained sandy clay loam till. The stand was almost pure trembling aspen except for several individual co-dominant paper birch (Betula papyrifera) trees. The shrub stratum included Vaccinium myrtilloides, Cornus canadensis, Linnaea borealis, and Rosa acicularis.

The jack pine control plot was located about 5 km north of these plots, 300 m west of highway 63 (Figure 1). The

plot was located on a gentle slope with a southeasterly aspect. The soil was a rapidly drained eluviated eutric brunisol developed in glaciofluvial sand. There was a sparse low shrub stratum of Vaccinium myrtilloides and a scattered lichen stratum principally of Cladina mitis.

The jack pine and aspen exposed plots were located about 30 m apart. They were both situated on moderately well-drained glacial till. The exposed jack pine plot consisted entirely of jack pine pine as the dominant tree species. The tall shrub stratum consisted of clumps of Alnus crispa and a few white spruce (Picea glauca) trees. A well-developed and prominent low shrub stratum was dominated by Ledum groenlandicum and Vaccinium myrtilloides.

The exposed aspen plot consisted of even-aged aspen. The tall shrub stratum was extensive and consisted almost entirely of Alnus crispa. The medium to low shrub stratum was very diverse and was dominated by Viburnum edule, Ribes triste and Rosa acicularis. The well developed herb stratum consisted principally of Linnaea borealis, Aralia nudicaulis and Cornus canadensis. The base of the aspen trees were covered by continuous mats of unidentified bryophytes.

The exposed black spruce plot was located about 2 km east of the jack pine and trembling aspen plots. It was situated in a dense stand of small black spruce on imperfectly drained glacial till. There were several white birch trees present and no tall shrubs. The intermittent

shrub stratum was dominated by Ledum groenlandicum. The bryophyte-lichen stratum formed a continuous ground cover, the principal species being Pleurocium scherberi, Hylocomium splendens and Cladina mitis.

3.2.2 Plot Description

Each plot (except the exposed black spruce plot) measured 30m x 30m (approximately 0.1 ha) and was divided into 36 quadrats of 5m x 5m. Twenty of these quadrats were selected using a random number table and a throughfall gauge was set up in the centre of each (Figure 2). The throughfall collectors consisted of five litre polyethylene bottles fitted with polyethylene funnels with an inside diameter of 21 cm. On plots where the crown closure was less than 80 per cent, throughfall gauges were placed under the tree nearest the centre of the quadrat. This was to ensure that there was an adequate number of collectors to obtain samples of throughfall. Ten stemflow collectors were attached to randomly selected trees in each experimental plot (Figure 2). The stemflow collectors consisted of split plastic piping fastened to the tree in a spiral fashion and sealed with an inert caulking compound. The piping led into 23-litre polyethylene "jerry" cans placed on the ground. Each device was fitted with a nylon screen to trap out insects and other debris. Two litter traps were randomly positioned in each plot (Figure 2). The litter traps were made up of 1m x 1m x 15cm wooden frames with fine (18 mesh) fiberglass

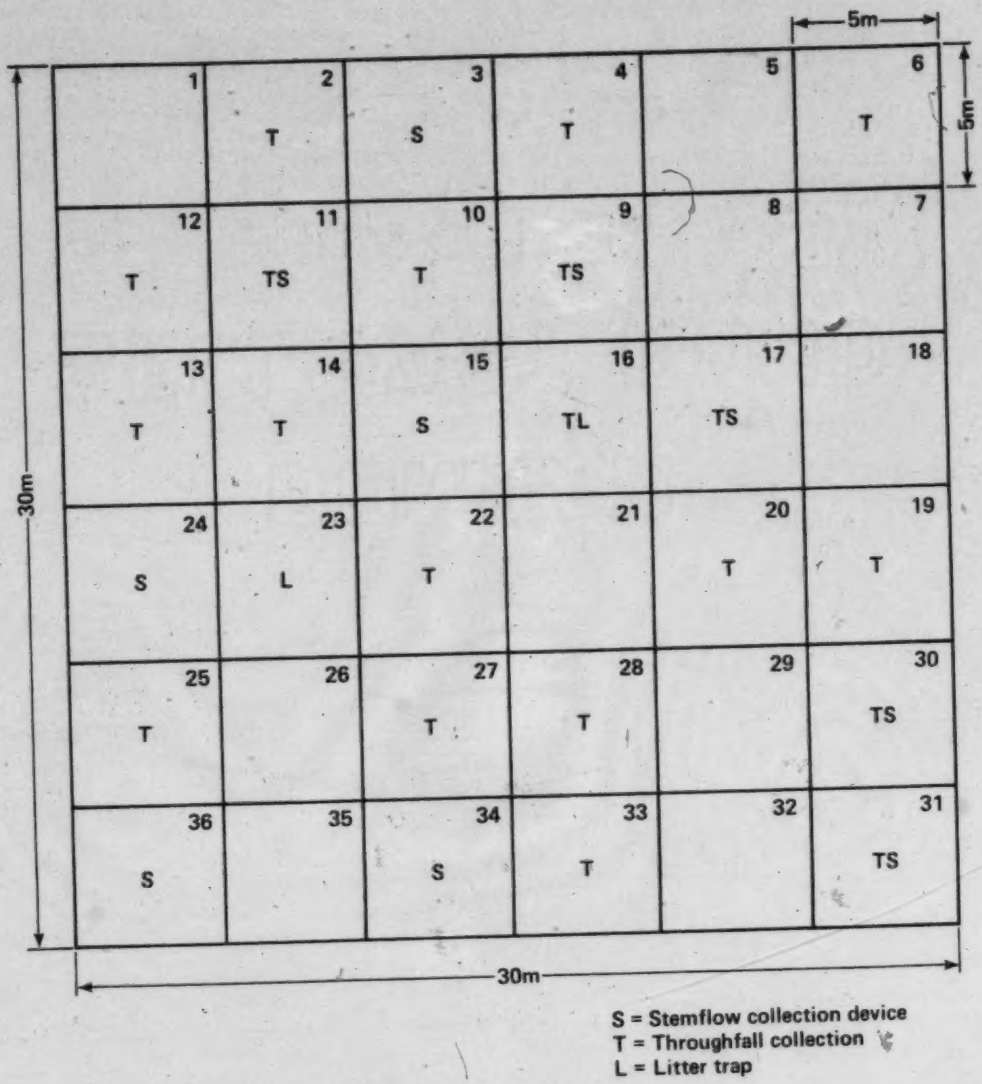


Figure 2. Layout of a typical plot used in the nutrient cycling study. The letters represent the randomly selected positions of the various collection devices.

screen bottoms. They were set on legs 15 cm above the ground surface. This number of collection devices per plot (20 throughfall, ten stemflow and two litter) was considered the minimum necessary for comparisons to be made between the plots at a reasonable confidence level (Kimmins 1973).

The black spruce exposed plot was 20m x 20m and had a narrow path cut through the centre and around the outside edges to provide access for sampling. This plot design was necessary because the density of the trees made a larger plot difficult to set up. Each 5m x 5m quadrat was divided into four subquadrats and a throughfall collector was positioned in two of these by random selection. The stemflow collection devices and litter traps were positioned as for the other plots.

Each plot had two rain gauges in a nearby clearing and a rain collection gauge to provide samples of incident rain for chemical analysis. The rain gauges were Taylor 11 inch (27.9 cm) "clear-vu" rain gauges (Sybon Corporation, N.C.). They were positioned approximately 40 cm above the ground surface. The rain sample collectors consisted of five-litre polyethylene bottles fitted with polyethylene funnels with an inside diameter of 21 cm. Each funnel was equipped with a fine mesh copper screen to prevent debris from contaminating the samples. The collection devices were placed inside wooden boxes attached to wooden stakes so that the gauges were approximately 40 cm above the ground surface.

Sulphation discs were also located at each plot in a wooden shelter box located in an adjacent opening. The sulphation discs consisted of plastic petri dishes containing lead dioxide on a support medium. The lead dioxide oxidizes gases such as sulphur dioxide and hydrogen sulphide to lead sulphate. This oxidation is known as total sulphation and is a useful means for the estimating the amount of sulphur gases in the ambient air.

3.2.3 Sample collection and analysis

3.2.3.1 Precipitation samples. Throughfall and stemflow were sampled approximately every two weeks for the control plots and monthly for the exposed plots. The exposed plots were sampled less frequently than the control plots because the only means of access to these plots was via helicopter. Sampling frequency was increased when there were frequent rain storms.

On each sample date the volume of water in each collector was recorded and a 250 ml sample taken. Rain water samples were collected in similar fashion. The filters were cleaned each time and 1 ml of chloroform was added to the polyethylene collection vessels and the sample bottles to prevent algal growth (Carlilse et al. 1967).

The Ca^{++}, Mg^{++}, Na^{+} and K^{+} concentrations were determined by atomic absorption using a Perkin-Elmer model

503 atomic absorption spectrophotometer with an air-acetylene flame. Samples for Ca^{++} and Mg^{++} determination were first diluted with 1 per cent La_2O_3 solution to reduce chemical interference. Detection limits for Ca^{++}, Mg^{++}, Na^{+} and K^{+} were 0.0005 ppm, 0.0001 ppm, 0.0002 ppm and 0.002 ppm respectively. Sulphate sulphur was determined using a modified version of the spectrophotometric method of Dean (1966).

The pH was determined using a Fisher Acumet 520 digital pH meter. Titratable acidity (total acidity) was determined by titrating a 25 ml aliquot of the degassed sample against 0.001 N KOH (standardized with H_2SO_4) to pH 7.00 using a combination glass electrode and a Fisher automatic titrimeter. It should be noted here that in any water sample there are two types of acidity that can be measured; free and total. Free acidity is a measure of the concentration of protons in solution regardless of source. They may originate from the dissociation of weak or strong acids. Free acid is therefore determined by measurement of the solution pH. Total acidity is determined by titration and is a measure of the concentration of protons, both those in solution and those still undissociated.

3.2.3.2 Litter samples. Litter samples were collected every month from all six study plots. The twigs, cones and leaves were air dried and stored in sealed plastic bags before analysis. The samples were then dried at 70°C in a forced

air furnace for 10-12 hours, cooled and the dry weight was recorded. The litter was then ground to 20 mesh using a Wiley mill. One gram of each sample (in duplicate) was ashed in a muffle furnace at 475°C for four hours. The ash was then dissolved in 5 ml of 20 per cent HCl and the solution was filtered (Whatman no. 42 filter paper). The filtrate was made up to 50 ml in a volumetric flask and the calcium, magnesium, potassium and sodium concentrations were determined by atomic absorption using the appropriate dilutions. Total sulphur was determined by the alkaline hypobromide oxidation method of Tabatabai and Bremner (1970).

3.2.3.3 Sulphation discs. Two sulphation discs were kept at each study plot. Each consisted of a plastic petri dish (4.8 cm inside diameter) and contained a PbO_2 compound which was prepared as follows: 576 g PbO_2 was mixed in a Waring blender with 36 g Gelman A glass fibre filters, 4 g gum tragacanth, 10 ml methanol and 700 ml water. The solution was made up to 2 litres and 5 ml of this material was transferred to each disc and then dried at 50°C for 12 hours (Huey 1968). The discs were sealed with a lid for transfer to the field.

Discs were left for an exposure period of one month at each plot before being replaced. They were analyzed for sulphur by digesting the insoluble lead sulphate (derived from reaction of sulphur gases in the air with PbO_2) with

sodium carbonate and then determining the SO4=-S by a modified version of Dean's (Dean 1966) method. The data were then expressed as mg SO3 equivalent per 100 cm^2 of plate surface area per day.

3.2.3.4 Soil samples. Soil pits were dug at each experimental plot and profiles described according to the conventions of the Canadian System of Soil Classification (Appendix 10.1). At the same time samples from each horizon were collected. These were air dried, then ground to pass through a 20 mesh sieve before analysis. The pH was determined using a Fisher Acumet pH meter. The soil to water ratios used were 20 g soil:20 ml water for mineral soil samples and 5 g soil:50 ml water for the organic soil samples.

Soluble sulphate was extracted by shaking the soil samples with 0.1 m CaCl2 for 30 minutes. The mixture was then filtered (Whatman no. 40 filter paper) and the SO4=-S content of the filtrate was determined by the method of Dean (1966). The extractant ratios used were 10 g soil:20 ml CaCl2 for mineral soil and 5 g soil:40 ml CaCl2 for organic soil. Soluble salts (Ca^{++}, Mg^{++}, K^{+} and Na^{+}) were determined from the saturated paste extracts by atomic absorption spectrophotometry (McKeague 1976).

Soil bulk density samples were taken with a custom made soil sampler with a 3.5 cm core diameter. Bulk density

samples of organic horizons were obtained by removing a 15 cm square block with a knife. Bulk density was calculated from the oven dry weight (105°C) and the core volume. Soil particle size analysis was performed using the hydrometer method (McKeague 1976). Soil colour was described on the air dry samples using the revised standard soil colour charts published by the Japanese Ministry of Agriculture and Forestry.

3.3 JACK PINE STEMFLOW STUDY

3.3.1 Experimental Design.

In June 1977, four plots were established to study the influence of sulphur dioxide emissions on the sulphur content and acidity of jack pine stemflow (Figure 1). Two control plots were established. One was located on the same plot as that used for the 1976 nutrient cycling study (Algar). The other control plot was located about 200 km SW of the emission source (May). Both plots were located at least 300 m from the highway to prevent contamination by motor vehicle exhaust fumes. The exposed plots were located at Muskeg Mountain about 38 km ENE of the emission source and at a location about 2.4 km ESE of the emission source (Steepbank 3).

Pure stands of jack pine were chosen for each plot. A description of the plots is given in Table 2. A Duncan's

multiple range test indicated that the mean tree diameter at Steepbank 3 was similar to that at May ($p<0.05$). The mean tree diameters at the other plots were not similar ($p<0.05$)

At each site stemflow collector devices were attached to five randomly selected trees. Rain gauges, rain sample collection gauges, and sulphation discs were set out at each site as for the 1976 nutrient cycling study (Section 3.2.2).

The plot at Steepbank 3 was located on moderately well-drained medium sand over tar sand. The two small trees studied had a mean age of 22 years while the three larger trees were about 36 years old. The plot at Muskeg Mountain was located on well-drained glacial till. The trees averaged 35 years old. The control jack pine site at Algar was described in detail above (Section 3.2.1). The trees at this site were about 120 years old. The control plot at May was on imperfectly drained glacial till and the trees were about 24 years old.

3.3.2 Sample collection and analysis

Jack pine stemflow was collected on three occasions during the summer of 1977: May 19-20, June 6-7 and July 3-5. At each sample period, all four plots were serviced. The amount of precipitation was recorded and a sample of rainwater was cclllected from the rain sample collection gauge. The volume of stemflow was recorded and a 250 ml sample taken for analysis. The pH, total acidity and SO4=-S

Table 2. Description of the four jack pine stemflow study sites.

Site	Distance From Source (km)	Direction From Source	Total Precipitation (mm)	Mean Tree Height (m)	DBH		
					Mean (cm)	Minimum (cm)	Maximum (cm)
Steepbank 3	2.4	ESE	51.7	13.2	16.8	11.3	23.0
Muskeg Mountain	38.0	ENE	49.3	7.7	12.9	12.1	14.0
Algar	101.0	SSW	43.0	15.9	21.4	18.3	28.1
May 2	200.0	SW	52.8	9.1	16.7	11.5	20.3

were determined on all samples as described for the nutrient cycling study (Section 3.2.3.1). Sulphation discs were replaced at each sample period at all four plots. These were analyzed as described above (Section 3.2.3.3).

3.4 DATA ANALYSIS

Most nutrient concentrations and pH values presented in this thesis are geometric means. That is, each concentration value is weighted according to the sample volume. To calculate means of pH values, pH numbers were first converted to their negative antilogarithms (hydrogen ion concentration). These were then multiplied by the sample volume and summed. This sum was divided by the sum of the sample volumes and the resulting concentration value was converted back to a pH value. This pH represents the strength of a solution of a completely ionized acid which could have brought the same amount of hydrogen ions per unit area to the ground as was brought by the rainfall, or throughfall etc. (Barret and Brodin 1955).

The volume corrected data could be calculated for single sample periods to give the amounts of nutrients leached at a given plot, but this mean value could not be used for a statistical comparison between the two sites. This is because on most occassions the throughfall or stemflow volume for a given species was significantly different ($p<0.05$) between sample periods and between the

control site and the exposed site for a given sample period. The data could not be corrected for these volume differences because the relationship between volume and the quantities of nutrients leached is not linear (Madgwick and Ovington 1959).

Principal component analysis was performed on the throughfall and stemflow data in order to determine whether there were differences in the factors associated with the leaching of cations from the tree crowns at the two sites. Such a distinction would allow hypotheses to be proposed regarding the mechanisms causing increased leaching of nutrients at the site exposed to higher levels of sulphur emissions. (Appendix 10.4).

All statistical analyses in this thesis were performed by using the Statistical Package for the Social Sciences (SPSS) (Nie et al. 1975).

3.5 TERMINOLOGY

There is considerable confusion in the literature on the terminolcgy used in the measurement of the distribution of water under tree crowns. (eg. Reynolds and Leyton 1963, Helvey and Patric 1965). The following definitions are used throughout this thesis.

Gross rainfall or incident precipitation (P): the rain falling on to the forest canopy. This was estimated by rain

gauges placed in a suitable open area near the study plots.

Throughfall (T): The portion of the incident precipitation reaching the ground either directly through the canopy spaces or as drip from the vegetation.

Stemflow (S): The portion of incident precipitation reaching the ground by flowing down the tree stems.

Net rainfall (R): The portion of incident precipitation reaching the ground in the form of throughfall and stemflow.

Interception loss (IL): The portion of incident precipitation retained by the tree canopy which is absorbed by the trees and/or evaporated directly into the atmosphere. This is equal to the difference between incident precipitation and net rainfall.

Interception storage capacity (IC): The maximum quantity of water which can be physically retained by the vegetation. This is equivalent to the amount of incident precipitation needed to saturate the forest canopy before net rainfall occurs.

4. DISTRIBUTION OF RAINFALL UNDER FOREST STANDS

4.1 RESULTS

4.1.1 Precipitation

The mean amount of precipitation for each individual sample period was similar for both control and exposed plots (Table 3). Individual rainfall events were sampled on most occasions. The range in storm sizes sampled was considerable (Table 3). The measurement period for the exposed black spruce plot was shorter than for the other plots because of difficulty in locating a suitable study area and because of problems in setting up the collection gauges (Section 3.2.2).

4.1.2 Throughfall

For trembling aspen the mean amount of throughfall was 84% of the incident rain at both sites (Tables 4 and 5). This corresponds to the range of 80-85% for hardwoods cited by Helvey and Patric (1965). For storms greater than 10 mm, the throughfall percentage is practically constant (at about 87%). The similarity for both aspen sites is also shown in the regression relationships between throughfall and precipitation given in Table 6. A linear relationship between throughfall and precipitation has been shown by a large number of researchers (eg. Voigt 1960, Pressland 1973,

Table 3. Amount of precipitation (mm) at the control site and the exposed site during the summer of 1976.

Experimental Plot	Duration of Measurement Period	Number of Sample Periods	Precipitation (mm)			
			Total	Mean Value Per Period	SD[1]	Min. - Max.
Control Aspen	24/6-2/10	8	318.4	39.8	43.6	3.7-138.8
Exposed Aspen	22/6-10/10	7	286.0	40.9	29.8	20.8-105.2
Control Pine	24/6-2/10	8	299.5	37.4	38.1	5.2-121.6
Exposed Pine	22/6-10/10	7	286.0	40.9	29.8	20.8-105.2
Control Spruce	24/6-2/10	8	328.5	41.1	43.6	3.7-138.8
Exposed Spruce	22/7-10/10	4	156.1	39.0	42.6	7.6-101.6

[1] SD=standard deviation

Table 4. Net rainfall, throughfall, stemflow and interception under a trembling aspen stand (control site) expressed as equivalent rainfall depth (mm) and percentage of gross rainfall.

Date	Gross Rainfall (mm)	Throughfall (mm)	Throughfall (%)	Stemflow (mm)	Stemflow (%)	Net Rainfall (mm)	Net Rainfall (%)	Interception (mm)	Interception (%)
June 18	28.3	24.8	87.6	1.5[1]	5.3	26.3	92.9	2.0	7.1
June 24	41.2	35.9	87.1	3.8[1]	9.2	39.7	96.4	1.5	3.6
June 29	30.4	27.6	90.8	1.9	6.3	29.5	97.0	0.9	3.0
July 16	48.8	43.5	89.1	3.6	7.4	47.1	96.5	1.7	3.5
July 23	10.1	7.1	70.3	1.0	9.9	8.1	80.2	2.0	19.8
July 30	34.9	29.7	85.1	3.5	7.8	33.2	95.1	1.7	4.9
Aug 4	3.7	2.9	78.4	0.2	5.4	3.1	83.8	0.6	16.2[2]
Aug 27	138.8	120.2	86.6	5.0[3]	3.6	125.2	90.2	13.6	9.8[3]
Sept 9	45.0	37.1	82.4	4.0[3]	8.9	41.1	91.3	3.9	8.7[3]
Oct 2[4]	6.7	4.8	71.6	0.5	7.5	5.3	79.1	1.4	20.9
Mean			84.2		7.1		90.6	1.6	7.8

1 Estimated
2 Collection gauges sampled during rain shower on previous sample date therefore interception is probably underestimated
3 Stemflow collection vessels overflowed therefore interception is overestimated
4 Freezing rain - no leaves left on the trees

Table 5. Net rainfall, throughfall, stemflow and interception under a trembling aspen stand (exposed site) expressed as equivalent rainfall depth (mm) and percentage of gross rainfall.

Date	Gross Rainfall (mm)	Throughfall (mm)	Throughfall (%)	Stemflow (mm)	Stemflow (%)	Net Rainfall (mm)	Net Rainfall (%)	Interception (mm)	Interception (%)
June 30	26.2	22.5	85.9	2.0[1]	7.6	24.5	93.5	1.7	6.5
July 15	41.6	36.7	88.2	4.2	10.1	40.9	98.3	0.7	1.7
July 29	43.0	36.4	84.7	3.5	8.1	39.9	92.8	3.1	7.2
Aug 10	20.8	15.7	75.5	1.6	7.7	17.3	83.2	3.5	16.8
Aug 25	21.4	17.9	83.6	1.7	7.9	19.6	91.6	1.8	8.4
Sept 8	105.2	90.6	86.1	6.7	6.4	97.3	92.5	7.9[2]	7.5
Mean			84.0		8.0		91.7	2.2	8.1

1 Estimated
2 Stemflow collection vessels overflowed therefore interception is overestimated

Table 6. Regression analysis of the relationships between throughfall (T), stemflow (S), per cent interception (I), and incident precipitation (P). Values are in mm.

Species and Site	Linear Regression Equation	Coefficient of Determination (r^2)	Standard Error of Estimate[1] (mm)	Degrees of Freedom
Control Aspen	T= -0.425 + 0.871P***	0.999	1.112	9
	S= 1.118 + 0.034P***	0.693	1.070	7
Exposed Aspen	T= -0.912 + 0.872P***	0.999	1.061	5
	S= 0.850 + 0.058P***	0.926	0.654	4
Aspen - Both Sites Combined	T= -0.587 + 0.871P***	0.999	1.040	15
	S= 1.135 + 0.041P***	0.720	1.046	12
Exposed Pine	T= -4.466 + 0.931P***	0.947	7.161	6
	S= 0.202 + 0.009P***	0.876	0.126	5
Control Spruce	T= -3.768 + 0.966P***	0.998	1.985	8
	S= 0.114 + 0.006P***	0.889	0.113	6
	logI= 0.142 + 0.352 logP***	0.789	0.112	6

*** Significant at $P < 0.001$
[1] Standard error of the residuals

Jackson and Aldridge 1973). The equation developed from the combined data from both aspen sites (T = -0.687 + 0.871P) agrees well with the generalized equation of Helvey and Patric (1965) (T = -0.787 + 0.901P) for estimates of growing season throughfall in mature, eastern hardwoods. Throughfall (T) and precipitation (P) are in mm.

Interception storage capacity or canopy saturation values cannot be measured directly. They can be determined approximately by extrapolation of the regression curves to T=0. These will only give general values since accurate determination would require measurements of small storm events, and Szabo (1975) has noted that the correlation between incident rain and throughfall is not linear for small storms. From the regression equations (Table 6) it can be seen that approximately 0.5mm and 1.0mm of precipitation are required to saturate the aspen canopies at the control site and exposed site respectively. This compares with the interception storage capacity values recorded by Zinke (1967) of 0.25-9.15mm for various hardwood and conifer species.

The amount of throughfall under jack pine at the exposed site was also relatively constant when expressed as a percentage of the incident rain (86%), but on several occasions at the control site the quantity of throughfall exceeded the incident rain (Table 7). This has been noted by several others workers (Ovington 1954, Voigt 1960, Pressland

Table 7. Net rainfall, throughfall, stemflow and interception under a jack pine stand (control site) expressed as equivalent rainfall depth(mm) and percentage of gross rainfall.

Date	Gross Rainfall (mm)	Throughfall (mm)	Throughfall (%)	Stemflow (mm)	Stemflow %	Net Rainfall (mm)	Net Rainfall (%)	Interception (mm)	Interception (%)
June 29	45.0	41.0	91.1	0.1[1]	0.2	41.1	91.3	3.9	8.7
July 16	45.4	38.4	84.6	0.1	0.2	38.5	84.8	6.9	15.2
July 23	8.8	6.3	71.6	0.0	0.1	6.3	75.0	2.5	28.4
July 30	31.5	32.1[2]	101.9	0.2	0.5	32.6	103.5	1.1	-3.5
Aug 4	5.2	3.6	69.2	0.0	0.0	3.6	69.2	1.6	30.8
Aug 27	121.6	129.9[2]	106.8	1.0	0.8	130.9	107.6	-9.3	-7.6
Sept 9	39.6	41.3[2]	104.3	0.3	0.7	41.6	105.1	2.0	-5.1
Oct 2	5.2	2.0	38.5	0.1	0.2	2.0	38.5	3.2	61.5
Mean			83.5		0.3		84.4	3.6	28.9 (16.1)[3]

[1] Estimated
[2] Throughfall exceeded gross rainfall. Refer to text for explanation
[3] Including negative values

1973). This anomaly could have arisen from errors in the throughfall gauge readings. Gauges located at the edge of the canopy at times received large volumes of water which could have run off the surface of the tree canopy. This "umbrella effect" would tend to cause an overestimation of the mean throughfall if a large portion of the throughfall gauges were located near the crown periphery. Alternatively, rain at an oblique angle may have been caught directly by the throughfall gauges without passing through the canopy. This is more likely to have occurred at the control site than the exposed site because of the lower crown cover at the control site. The control jack pine site was located on a hill-side with a southwesterly aspect. Rain storms accompanied by wind from this direction could cause rain to fall at an oblique angle to the trees. It is interesting to note that on the three occasions when throughfall exceeded incident rain the percentage stemflow was unusually high (Table 7). This could be explained by the wind driven rains impinging directly onto the tree trunks. Black (1957) noted that stemflow was greatest during storms accompanied by a high wind.

The percentage of precipitation reaching the ground as throughfall for jack pine at the exposed site (86%) was similar to that for aspen (Tables 4 and 5). Henderson et al. (1977) similarly found no difference in the amount of throughfall under pine and hardwood stands. The linear relationship between jack pine throughfall and incident

precipitation is shown by the regression equation in Table 6. The interception storage capacity for jack pine at the exposed site was about 5.0mm (Table 8), considerably higher than for aspen.

Throughfall under black spruce at the control site averaged 76% of incident precipitation (Table 9). This is slightly less than 81% reported for black spruce by Mahendrappa (1974). There were several occasions when throughfall under black spruce at the exposed site exceeded incident precipitation (Table 10). This may also have been because of the 'umbrella effect' of the tree canopies on throughfall received by gauges located at the crown periphery. Gusting wind conditions may have increased recorded throughfall by shaking branches and causing stem drip. In addition, trees at the exposed black spruce site were small and the gauges were located just under the relatively thin canopy. The linear regression relationship between incident precipitation and throughfall for black spruce at the control site is shown in Table 6. Interception storage was approximately 3.9 mm.

4.1.3 Stemflow

Stemflow averaged 7% of incident precipitation at the aspen control site and 8% at the aspen exposed site (Tables 4 and 5). This is larger than the 1.5 - 2.2% reported for largetooth aspen by Clements (1971). However, Mahendrappa

Table 8. Net rainfall, throughfall, stemflow and interception under a jack pine stand (exposed site) expressed as equivalent rainfall depth (mm) and percentage of gross rainfall.

Date	Gross Rainfall (mm)	Throughfall (mm)	Throughfall (%)	Stemflow (mm)	Stemflow (%)	Net Rainfall (mm)	Net Rainfall (%)	Interception (mm)	Interception (%)
June 30	26.2	20.5	78.2	0.0[1]	0.1	20.5	78.2	5.8	22.0
July 15	41.6	35.9	86.3	0.1	0.2	36.0	86.5	5.6	13.5
July 29	43.0	36.3	84.4	0.0	0.1	36.3	84.4	6.7	15.5
Aug 10	20.8	17.1	82.2	0.0	0.1	17.1	82.2	3.0	14.8
Aug 25	21.4	18.9	88.3	0.0	0.0	18.9	88.3	2.6	12.0
Sept 8	105.2	100.1	95.2	0.8	0.8	100.9	95.9	4.3	4.1
Mean			85.8		0.2		85.9		13.7

[1] Estimated

Table 9. Net rainfall, throughfall, stemflow and interception under a black spruce stand (control site) expressed as equivalent rainfall depth (mm) and percentage of gross rainfall.

Date	Gross Rainfall (mm)	Throughfall (mm)	Throughfall (%)	Stemflow (mm)	Stemflow (%)	Net Rainfall (mm)	Net Rainfall (%)	Interception (mm)	Interception (%)
June 24	41.2	35.3	85.7	-	-	35.3	85.7	5.9	14.3
June 29	30.4	22.4	73.7	-	-	22.4	73.7	8.0	26.3
July 16	48.8	40.8	83.6	0.0	0.04	40.8	83.6	8.0	16.4
July 23	10.1	6.6	65.3	0.0	0.00	6.6	65.3	3.5	34.7
July 30	34.9	29.7	85.1	0.0	0.09	29.7	85.1	5.2	14.9
Aug 4	3.7	1.6	43.2	0.0	0.00	1.6	43.2	2.1	56.8
Aug 27	138.8	131.4	94.7	0.8	0.61	132.2	95.2	6.6	4.8
Sept 9	45.0	41.4	92.0	0.1	0.02	41.5	92.2	3.5	7.8
Oct 2	6.7	4.2	62.7	0.0	0.00	4.2	62.7	2.5	37.3
Mean			76.2		0.13		76.3	5.0	23.7

Table 10. Net rainfall, throughfall, stemflow and interception under a black spruce stand (exposed site) expressed as equivalent rainfall depth (mm) and percentage of gross rainfall.

Date	Gross Rainfall (mm)	Throughfall (mm)	Throughfall (%)	Stemflow (mm)	Stemflow (%)	Net Rainfall (mm)	Net Rainfall (%)	Interception (mm)	Interception (%)
June 29	38.6	36.3	94.0	0.0	0.0	36.3	94.0	0.5	1.3
July 29	28.4	23.0	81.0	0.2	0.8	23.2	81.7	5.2	18.3
Aug 10	7.6	7.9[1]	-	0.0	0.1	-	-	-	-
Aug 25	18.5	18.9[1]	-	0.1	0.4	-	-	-	-
Sept 8	101.6	85.2	83.9	2.3	2.21	87.4	86.0	14.2	14.0
Oct 10	31.8	36.1[2]	-	0.1	0.3	-	-	-	-
Mean			86.3		0.6		87.2		11.2

[1] Throughfall exceeded gross rainfall. Refer to text for explanation
[2] Rain and snow

(1974) reported a value of 6.1% for largetooth aspen, and it is similar to reports of 9.6% for American beech (Voigt 1960) and 11.5% for European beech (Nihlgard 1970) which have bark characteristics similar to trembling aspen. The high amount of stemflow recorded for aspen is undoubtedly due to tree form, with branches tending tc grow upward rather than outward, and to the smooth bark on the tree trunks.

Generally, aspen stemflow per sample period increased with increasing basal area of the tree (Figure 3). This relationship tended to be curvilinear for small trees. Stemflow tended to be independent of tree size for the larger trees, for small storms. Pressland (1973) noted a curvilinear regression for the smaller trees, while linear regressions described the relationship for the larger trees of Mulga (Acacia aneura). Mulga has a large proportion (18%) of the rainfall channelled to the ground as stemflow, as does aspen. Such relationships have also been noted by Clements (1971) and White and Carlilse (1968). A curvilinear relationship between stemflow and incident precipitation could explain the positive Y intercept in the linear regression equation developed for aspen which is given in Table 6. Because of the positive Y intercept, the amount of rain needed before stemflow begins cannot be estimated from the regression equations. The results indicate (Table 4) that measurable stemflow occurs after 3.7mm of rain so the amount of precipitation required to wet the canopy

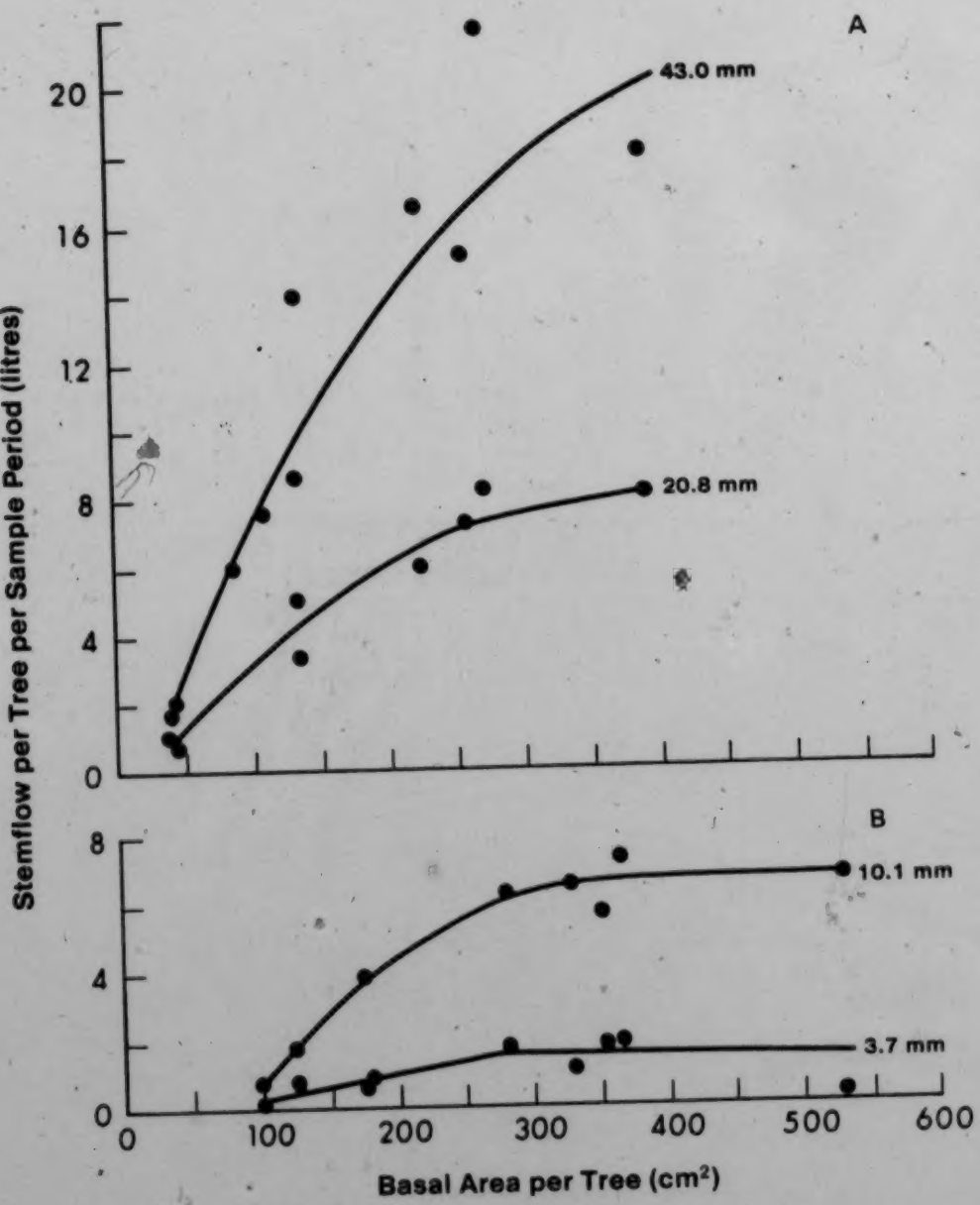


Figure 3 Volume of stemflow per tree from trembling aspen for large storms (A) and small storms (B). Note the curvilinear relationship of stemflow volume to basal area.

components before stemflow occurs must be less than 3.7mm.

The quantities of stemflow for jack pine tended to be considerably less than for aspen (Tables 7 and 8). Stemflow averaged 0.2-0.4% of incident precipitation for jack pine compared to 7-8% for trembling aspen. This is partly due to the different tree form in jack pine. Branches tend to grow outward rather than upward. In addition, the rough bark of jack pine would have a higher storage capacity (greater surface area for a given stem size) than aspen. This may also explain the lower stemflow recorded for jack pine. Voigt (1960) has noted that stemflow actually drops in a diffuse pattern around rough barked trees rather than adhering to and flowing down the trunks. By increasing the width of the stemflow collectors from 1 to 19 inches he found stemflow catch increased by 50%. The rather narrow stemflow gauges used in this study (approx. 6cm wide) may have underestimated stemflow on jack pine to some extent. Stemflow was recorded in some of the gauges after 5.2 mm of rainfall. This compares with 5.1mm for ponderosa pine (Pinus ponderosa) (Orr 1972) and 7.6mm for canary pine (Pinus canariensis) reported by Kittredge et al. (1941).

Stemflow at the black spruce control site averaged only 0.1% of incident precipitation whereas at the exposed site stemflow averaged 0.6% of incident precipitation (Tables 9 and 10). These differences reflect the nature of the tree crowns at both sites. Trees at the exposed site were

generally smaller and had a less dense crown than trees at the control site. At the exposed site incident rain may have been collected as stemflow in the smaller sized trees, causing stemflow to be slightly overestimated. In either case the stemflow from spruce is very small and in agreement with values reported elsewhere (Mahendrappa 1974).

4.1.4 Net Rainfall and Interception

Net rainfall averaged 92% and 91% for exposed site aspen and control site aspen respectively. Interception was also similar for both sites averaging about 8% with a range of 1.7 to 20.9% (Tables 4 and 5). Clements (1971) reported an average of about 8% for largetooth aspen for a similar four month period. The values reported here are lower than other reported values for trembling aspen. Dunford and Niedehof (1944) reported about 16% interception for 32 year old aspen and Molchanov (1963) reported 19-30% interception for aspen 37 to 43 years old.

Net rainfall generally increased with increasing amounts of precipitation per sample period (storm size) as would be expected, and correspondingly, per cent interception decreased. It is interesting to note that interception was still high (21%) when the trees were leafless (Tables 4 and 5).

Interception by jack pine averaged 13.7% over the summer period at the exposed site (Table 8). At the control

site interception averaged 29% when periods of negative interceptions are excluded and 16% when they are included (Table 7). These values correspond to 18.7% reported for red pine (Pinus resinosa) by Voigt (1960) and 17 to 28% for canary pine (Kittredge et al. 1941). Mitchel (1930) reported a value of 21% for 50 year old jack pine in Wisconsin. Throughfall gauges not located directly beneath the tree crowns also showed interception. That is, they received less precipitation than gauges located in the nearby clearing. Interception was larger for lower storm sizes and generally decreased with increasing amount of precipitation (Tables 7 and 8).

Interception averaged 24 percent at the black spruce control site (Table 9). This is in agreement with results reported for other spruce stands (Mina 1965, Nihlgard 1970, Mahendrappa 1974). Interception on the exposed site was much lower due to reasons explained earlier (Section 4.1.2). A curvilinear relationship resulted from a plot of interception versus precipitation on the black spruce control plot. A good linear fit was obtained when the data were transformed logarithmically (Table 6). The relationship between incident precipitation and per cent interception was:

$$I(\%) = 1.39 \times P^{0.35} \qquad (r^2=0.789)$$

where I = per cent interception

P = incident precipitation in mm

This equation was obtained by rearranging the regression

equation given in Table 6.

4.1.5 Sampling Intensity

The planning of most precipitation studies suffers from a lack of information on the spatial and temporal variance of throughfall and stemflow. Researchers have used a wide variety of collection vessels to sample throughfall including troughs (Kittredge et al. 1941, Delfs 1955, Reigner 1964), standard rain gauges (Reynolds and Leyton 1963), and polyethylene funnels (Eaton et al. 1970, Voigt 1960). The number of fixed gauges has ranged from 1 to 30 and roving gauges from 1 to 20 (Kimmins 1973). It was, therefore, of interest to determine the degree of precision obtained by the sampling technique employed in this study.

Table 11 shows the standard error expressed as per cent of the mean for the value of throughfall and stemflow for small, medium and large sized storms at each experimental plot. Aspen throughfall measurements were subject to standard errors of less than five per cent and variability decreased with increasing amount of precipitation. The same was true for the other two species. Other researchers have noted a curvilinear decrease in coefficients of variation with increasing precipitation (Pressland 1973, Kimmins 1970). The standard errors for pine and spruce throughfall were higher, as would be expected from the greater variability in crown cover (Helvey and Patric 1965). The

Table 11. The number of throughfall and stemflow gauges required to make the 95% confidence interval about the mean, equal to 10% of the mean.

Site and Species	Precipitation	Standard Error[1]		Number of Gauges Required[2]			
		Throughfall	Stemflow	Throughfall		Stemflow	
	(mm)	(%)	(%)				
Control Aspen	10.1	3.3	17.2	6	(14.8)	80	(54.3)
	48.8	2.9	14.3	5	(13.2)	55	(45.2)
	138.8	2.6	-	3	(9.8)	-	-
Exposed Aspen	20.8	3.4	21.1	4	(12.1)	96	(59.7)
	43.0	2.6	19.6	3	(11.2)	104	(62.0)
	105.2	2.4	8.5	2	(8.3)	-	-
Control Pine	8.8	11.6	17.7	54	(44.7)	85	(56.0)
	45.4	4.9	33.8	9	(17.8)	309	(106.8)
	121.6	3.5	22.8	4	(12.7)	113	(64.6)
Exposed Pine	20.8	9.5	25.9	34	(35.5)	182	(81.9)
	43.0	8.0	35.4	26	(31.0)	339	(112.0)
	105.2	6.0	6.6	13	(22.3)	11	(20.1)
Control Spruce	10.1	8.3	26.6	36	(36.4)	172	(79.7)
	48.8	6.6	32.5	22	(28.7)	257	(97.5)
	138.8	3.6	21.3	7	(15.9)	110	(63.9)
Exposed Spruce	7.6	6.5	53.5	23	(28.9)	544	(141.8)
	28.4	11.0	61.1	33	(34.7)	808	(172.8)
	101.6	6.9	42.4	26	(30.9)	390	(120.0)

[1] Expressed as percentage of the mean.

[2] Number of gauges required $\frac{t^2 \times (CV)^2}{C^2}$. CV value is given in brackets

where: CV = Coefficient of Variation, t = 1.645 (p=0.10 for infinite population)
C = desired confidence interval (10%) as percentage of mean.

number of collectors required to make the 95% confidence interval about the mean, equal to ten per cent of the mean, was calculated (Table 11). Only the aspen throughfall gauges were of sufficient number to satisfy this requirement.

A large number of stemflow collectors is required to obtain the desired level of precision. Szabo (1975) also obtained high coefficient of variation values (20-70%) for stemflow.

The purpose of this study was to compare differences between sites over the summer period rather than monitor individual storm events. In some cases roving gauges may reduce the variance in throughfall volume (Reynolds and Leyton 1963, Wilm 1943). However, for short term studies a large number of collections would still be required and in some cases roving gauges may yield inaccurate results (Kimmins 1973).

4.2 DISCUSSION

Determination of the amounts of water reaching the soil in forest stands is important as it is this water which can be used by plants for growth or which can supply man's water needs. This water is also the vehicle for nutrient cycling via throughfall and stemflow.

The average net precipitation received under the forest canopy of the three forest types studied was: trembling

aspen (91%), jack pine (85%) and black spruce (81%). The largest amount of water reaching the forest floor was therefore found under trembling aspen. The least was found under black spruce. This high interception loss for black spruce is probably not important for this species as it usually grows on moist sites.

Researchers frequently disregard stemflow in water budget studies because of measurement difficulties. This study shows that stemflow can be a significant proportion of the water reaching the soil particularly for aspen. Stemflow is also an important consideration in the moisture economy of trees since the water is distributed directly into the rooting area of each tree.

Gaiser (1952) indicated that old root channels are relatively more permeable to water than the surrounding soil. Such channels could serve as pathways for rapid movement of free water in the soil profile both vertically and horizontally. Stemflow may serve as the principal point of entry into such a network (Voigt 1960). Beasley (1976) suggested that interconnected channels through the soil formed by decayed roots, could explain his observations that subsurface flow often began shortly after rainfall began, even when there was neither saturation at the point of outflow nor high antecedent soil moisture. He also found a similarity in the timing of subsurface and channel flows. This suggests that in some soils, stemflow may enter streams

relatively quickly without reaching chemical equilibrium with the soil.

Throughfall was also observed to result in an uneven distribution of rainfall, with the gauges located at the crown periphery (particularly for jack pine and spruce) often receiving greater amounts than similar gauges located in an open area. The distribution of throughfall over the forest floor was most variable in jack pine and black spruce and least variable in trembling aspen. Variability between the two study plots for each species was least for aspen and greatest for black spruce. This uneven distribution of moisture might be expected to influence the micro-environment of the forest floor. Indeed, several researchers have recognized stemflow and throughfall as important factors contributing to local soil variability (Mina 1967, Gersper and Holowaychuk 1971).

The regression equation developed for estimating aspen throughfall (T) from measurements of gross rainfall (P) corresponds remarkably well with that developed by Helvey and Patric (1965) from 12 separate studies in the eastern United States. This suggests that the regression equation developed for estimating aspen throughfall in this study could be used by other researchers for estimating throughfall in similar trembling aspen stands elsewhere in Alberta.

5. NUTRIENT TRANSFER FROM FOREST CANOPY TO SOIL

5.1 RESULTS

5.1.1 Litter Production

Litter production (oven dried weight) by the control aspen stand compared tc the exposed aspen stand was 1677 to 1869 kg/ha/yr. This is in close agreement with values of 1623 and 1778 kg/ha/yr for trembling aspen stands of similar density in Alaska (Van Cleve and Noonan 1975) and 1900 kg/ha/yr for leaves of Populus tremula at 59° N in Sweden (Anderson and Enander 1948). In relation to litter production by forests in other major climatic zones of the world, these values are about midway between average litter production in the cool temperate zone (3500 kg/ha/yr) and arctic-alpine zone (1000 kg/ha/yr) forests (Bray and Gorham 1964). The values reported here refer only to leaves and small twigs. If adjusted for branch fall of 15%, as found by Van Cleve and Noonan (1975) in a 50 year aspen stand in Alaska, then total litter production would be approximately 1930 kg/ha/yr and 2150 kg/ha/yr for control and exposed sites, respectively. This corresponds well with the total litter production of two metric tons/ha/yr predicted by Bray and Gorham (1964, Figure 1, pg 128) for forests at 57° N latitude.

At the control site, jack pine litterfall supplied 785

kg/ha of organic matter between July 23 and October 2. Assuming that the rate of litter production was the same in June as in July then production for the period June 24 to October 2 amounted to 806 kg/ha. According to Foster and Gessel (1972) approximately 75% of annual litter production in jack pine occurs between June and November. Using this figure, the approximate annual litter production for jack pine in this study would be 1050 kg/ha/yr. This is considerably less than 3729 kg/ha/yr for a 30 year old jack pine stand in Ontario (Foster 1974). It is also less than the 2100 kg/ha/yr (Alway and Zon 1930) and 1730 kg/ha/yr (Tappeiner and Alm 1972) reported for jack pine in the north central United States. It is, however, close to the 1200 kg/ha/yr reported for Pinus contorta at an elevation of 3000 m in the United States (37° N) by Jenny et al. (1949) These differences are probably due to the poor soil, the low stand density, and the short growing season at this site.

Black spruce at the control site produced an estimated 780 kg/ha of litter over the summer period. Although it is difficult to make a comparison with the limited data from this study, it appears that black spruce litter production at this site is considerably less than for other spruces reported by Bray and Gorham (1964).

5.1.2 Litter Nutrient Content

The mean nutrient content of litter for the three

species studied is given in Table 12. The order of concentration of nutrient elements in the three species was:

aspen > spruce > pine

for all nutrients except magnesium which was higher in pine than spruce. Nutrient content of jack pine litter varied over the study period (Table 12). Early in the autumn, litter had higher concentrations of the mobile elements, sulphur and pctassium, and lower concentrations of immobile calcium, relative to litter falling in the late autumn. Foster and Gessel (1972) also noted a marked increase in calcium concentration and a slight decrease in potassium concentration in jack pine litter in the late autumn. The sulphur content of jack pine litter decreased throughout the growing season (Table 12). Foster and Gessel (1972) observed a similar decrease for nitrogen in jack pine. Both nitrogen and sulphur could be translocated out of the tree crown towards the end of the growing season. The decrease in potassium and increase in calcium has been attributed to leaching (Gosz et al. 1972). Potassium is readily leached from attached leaves after the abscission layer is formed, hence, the lower potassium concentrations in late autumn litter. Calcium is leached more slowly than other matter (Tukey 1970), hence, the leaves lose weight and increase in calcium concentration. Spruce litter also showed an increase in calcium and magnesium and a decrease in sulphur concentrations in late autumn. Potassium, however, increased. Aspen litter showed a marked increase in calcium

Table 12. Nutrient content of tree litter expressed as per cent oven dry weight (O.D.W).

Sample date	Na (%)	K (%)	Ca (%)	Mg (%)	S (%)
		Jack Pine			
August 27	0.013	0.110	0.430	0.805	0.054
September 9	0.004	0.100	0.405	0.595	0.048
October 2	0.004	0.078	0.565	0.720	0.035
Mean	0.007	0.096	0.467	0.707	0.046
		Trembling Aspen			
September 9	0.024	0.420	0.840	0.855	0.168
October 2	0.018	0.560	1.235	1.805	0.214
Mean	0.021	0.485	1.038	1.330	0.191
		Black Spruce			
August 27	0.005	0.100	0.800	0.570	0.100
September 9	0.019	0.130	0.420	0.525	0.064
October 2	0.008	0.200	0.940	0.717	0.065
Mean	0.011	0.125	0.743	0.555	0.076

and magnesium. Presumably these elements accumulate in the leaf until abscission (Gosz et al. 1972). The order of element content for each species was:

trembling aspen: Mg > Ca > K > S > Na

jack pine: Mg > Ca > K > S > Na

black spruce: Ca > Mg > K > S > Na

The high magnesium content of the litter in all three species may reflect the influence of soil composition (Appendix 10.2), although the influence of soil chemical factors on nutrient content of trees has been discounted by Bard (1945) and Remezov et al. (1955).

Nutrient content of the litter of jack pine, aspen and black spruce in comparison to values reported for similar species is shown in Table 13. Jack pine generally had similar levels of sodium, calcium, and sulphur with slightly lower potassium and higher magnesium. Aspen was similar for all the elements determined except magnesium which was much higher. This was also the case for spruce.
These differences reflect the selective absorptive capacity of each species and physiological differences (Madgwick and Ovington 1959).

5.1.3 Nutrient Inputs in Precipitation

The nutrient content of precipitation at the control site is shown in Table 14. The mean nutrient concentrations (ppm) of sodium (0.14), potassium (0.17), calcium (0.44),

Table 13. Comparison of the nutrient content of litter reported by various researchers. Values are expressed as per cent over dry weight (O.D.W).

Species	Age (years)	Location	Na (%)	K (%)	Ca (%)	Mg (%)	S (%)	Reference
P. banksiana	120	Alta, Canada	0.01	0.10	0.47	0.71	0.05	This study
P. banksiana	30	Ontario, Canada	-	0.14	0.35	0.05	-	Foster (1974)
P. banksiana	30	Minnesota	-	0.05	0.56	-	0.07	Alway and
P. banksiana	55	Minnesota	-	0.08	0.81	-	0.10	Zon (1930)
P. taeda	62	North Carolina	0.01	0.12	0.37	0.11	-	Wells et al. (1972)
P. resinosa	25	New York	-	0.35	0.58	0.18	-	Chandler (1944)
P. radiata	44	New Zealand	0.10	0.30	0.54	0.11	-	Will (1959)
P. tremuloides	69	Alta., Canada	0.02	0.49	1.04	1.33	0.19	This study
Q. petraea	40-120	England	0.04	0.27	0.62	0.10	-	Carlisle et al. (1966)
P. tremuloides	50	Alaska	-	0.49	2.40	0.35	-	Van Cleve and
P. tremuloides	120	Alaska	-	0.28	1.73	0.33	-	Noonan (1975)
P. mariana	73	Alta., Canada	0.01	0.13	0.74	0.56	0.08	This study
P. abies	24	New York	-	0.39	1.96	0.23	-	Chandler (1944)

Table 14. Nutrient content of precipitation at the control aspen site during the period 24 June to 2 October, 1976.

Sample Date	Amount	Na		K		Ca		Mg		SO4=-S	
	(mm)	ppm	kg/ha	ppm	kg/ha	ppm	kg/ha	ppm	kg/ha	ppm	kg/ha
June 29	30.4	0.08	0.024	0.11	0.033	0.38	0.116	0.02	0.006	0.25	0.076
July 16	48.8	0.10	0.049	0.23	0.112	0.40	0.195	0.06	0.029	0.19	0.093
July 23	10.1	0.34	0.034	0.56	0.057	0.64	0.065	0.10	0.010	0.18	0.018
July 30	34.9	0.10	0.045	0.07	0.032	0.47	0.212	0.18	0.081	0.08	0.036
August 28	138.8	0.15	0.208	0.07	0.097	0.40	0.555	0.08	0.111	0.00	0.000
September 9	45.0	0.12	0.054	0.07	0.032	0.42	0.189	0.06	0.027	0.25	0.113
October 2	6.7	0.10	0.007	0.08	0.005	0.36	0.024	0.04	0.003	-	-
Totals	314.7		0.42		0.37		1.36		0.27		0.34
Mean		0.14		0.17		0.44		0.08		0.16	
SD[1]		0.09		0.18		0.10		0.05		0.10	

[1] Standard Deviation

magnesium (0.8) and sulphate sulphur (0.16) were higher (except sulphur), but the relative concentrations of each element were similar to those reported for a forested area at Hubbard Brook, New Hampshire, by Eaton et al. (1972). Their reported values were; sodium (0.06), potassium (0.07), calcium (0.16), magnesium (0.03) and sulphate sulphur (2.7). The higher sulphate sulphur at Hubbard Brook was attributed to contamination from pollution. In both cases calcium was the predominant cation. The average Ca/Mg ratio at the control site in this study was 5.5 reflecting the continental nature of the air masses (Section 2.1). The quantities of nutrients brought down in rain over the summer were not insignificant. The quantity of calcium in rain (1.36 kg/ha) was quite large and perhaps reflects the nature of the soils in the region. There were no apparent seasonal trends in the quantities of nutrients added through precipitation. The amounts of nutrients deposited in rain at each plot are given in Appendix 10.3.

5.1.4 Addition of Nutrients to the Forest Floor.

The relative contributions of jack pine throughfall, stemflow and litterfall to the amount of nutrients returned to the forest floor are shown in Tables 15 and 16. Note that the amounts of nutrients in throughfall and stemflow include elements added to the ecosystem in precipitation. Table 15 includes data for the period July 23 to October 2, for which accurate litterfall data were available. Table 16 shows a

comparison of the amounts of nutrients transported by each process over the summer period. The amounts of nutrients in litter were calculated assuming a similar rate of litterfall in June and July and assuming that the per cent mineral content of the litter was the same for both months.

Jack pine stemflow contributed only about one per cent of the nutrients returned to the forest floor, considerably less than for throughfall (Table 15). Almost all the sodium reaching the forest floor was via throughfall, and this was largely derived from the incident precipitation (Table 16). Litterfall was the most important source of calcium and magnesium, although, significant amounts of each were present in throughfall. Throughfall supplied approximately 70% of the potassium to the ground, more than double that supplied by litterfall. Greater quantities of potassium in throughfall than in litterfall have also been reported for jack pine (Foster 1974), Douglas-fir (Cole et al. 1967) and radiata pine (Will 1959). The order of return of nutrients from all sources to the soil was Ca > Mg > K > Na which differed from the order for jack pine (Ca>K>Mg) given by Foster (1974), presumably, because of the higher amount of magnesium returned in the litter at this study site. The order of return of nutrients in throughfall and stemflow was similar for both studies.

Aspen litterfall contributed nearly all of the calcium and magnesium returned to the forest floor during the summer

Table 15. Natural addition of nutrients to the forest floor of a jack pine ecosystem (control site) for the period 23 July to 2 October, 1976.

	Na		K		Ca		Mg		SO4=-S		Total S
	kg/ha	% of total	kg/ha	% of total	kg/ha	% of total	kg/ha	% of total	kg/ha	% of total	kg/ha
Throughfall	0.424	90	1.054	59	2.246	36	0.629	9.9	0.823		
Stemflow	0.006	1	0.020	1	0.083	1	0.010	0.1	0.037		
Litterfall	0.042	9	0.722	40	3.976	63	5.714	90.0			0.325
Total	0.472		1.796		6.305		6.353				

Table 16. Natural addition of nutrients to the forest floor of jack pine, trembling aspen and black spruce ecosystems for the 24 June to 2 October, 1976.

	Na		K		Ca		Mg		SO4=-S		Total S
	kg/ha	% of total	kg/ha	% of total	kg/ha	% of total	kg/ha	% of total	kg/ha	% of total	kg/ha
Jack Pine											
Throughfall	0.582	92	1.795	70	3.468	45	0.910	13	1.655		
Stemflow	0.007	1	0.023	1	0.009	2	0.012	1	0.048		0.337
Litterfall[1]	0.045	7	0.745	29	4.068	53	5.885	86			
Total	0.634		2.563		7.635		6.807				
Trembling Aspen											
Throughfall	0.281	47	3.146	25	2.187	5	0.372	1	0.787		
Stemflow	0.024	3	0.483	4	1.664	4	0.231	1	0.095		3.53
Litterfall	0.299	50	9.057	71	40.390	91	29.100	98			
Total	0.604		12.686		44.241		29.703				
Black Spruce											
Throughfall	0.303	71	2.852	67	2.152	25	0.502	9	1.957		
Stemflow	0.004	0	0.082	2	0.141	1	0.034	0	0.123		
Litterfall	0.124	29	1.318	31	6.388	74	5.084	91			
Total	0.431		4.252		8.681		5.620				

[1] Calculated assuming a similar rate of litterfall in June as in July and assuming that the per cent mineral content of the litter was the same for both months.

(Table 16). A considerable amount of sodium was also transferred in the litter, contrary to the findings for jack pine. Potassium and sodium were the predominant elements returned in aspen throughfall as in jack pine throughfall. Aspen throughfall, however, was less important as a transfer nutrient mechanism, in comparison to litterfall, than was jack pine throughfall. Aspen stemflow was relatively unimportant in the addition of nutrients to the forest floor in comparison to throughfall and litterfall. Stemflow returned nearly as much calcium as throughfall, however. This may reflect the high calcium content of the leaf leachate that has been channeled down the tree trunk or the calcium content of the bark. The order of addition of nutrients tc the forest floor was:

Ca > Mg > K > Na

which was the same as for jack pine and reflects the importance of litter to the return of nutrients in the aspen ecosystem.

The relative quantities of nutrients returned in black spruce throughfall, stemflow, and litterfall are shown in Table 16. As for jack pine, litterfall was the most important source of calcium and magnesium. Throughfall contributed more than twice the amount of potassium than litterfall. Potassium was the nutrient element returned in greatest quantity in stemflow. A significant amount of magnesium (25%) was returned to the forest floor in throughfall.

The order of the return of nutrients (Ca>Mg>K>Na) for spruce was the same as for aspen and pine. Relatively more potassium was returned in spruce than in the other two ecosystems. The quantity of sodium returned was similar for the three forest types since precipitation was the primary source for this element. The amounts of potassium, calcium and magnesium returned over the summer period were smaller for pine and spruce than for aspen.

5.1.5 Nutrient Flux from Forest Vegetation to Forest Floor

Approximately 62% of the calcium and 86% of the magnesium was returned from jack pine trees to the forest floor in the litter whereas 71% of the sodium and 67% of the potassium was recycled in throughfall and stemflow (Table 17). A large portion of the calcium content of the throughfall and stemflow was derived from incident precipitation. Leaching from the tree crowns was the primary means of recycling potassium in the pine ecosystem.

Sodium was removed from precipitation by the aspen canopy and consequently litter was the principal means of recycling sodium. Absorption of sodium by tree crowns has also been noted in radiata pine (Will 1959). Litter was also the primary means of recycling potassium, calcium, and magnesium. Potassium was the nutrient element recycled to the greatest extent in throughfall and stemflow (26%), followed by calcium (6%).

Table 17. The cycling of nutrients from forest canopy to the forest floor during the period 24 June to 2 October, 1976.

	Na		K		Ca		Mg		SO4=-S
	kg/ha	% of total	kg/ha	% of total	kg/ha	% of total	kg/ha	% of total	kg/ha
Control Pine									
Precipitation	0.47		0.30		1.04		0.09		0.25
Net Precipitation[1]	0.59		1.82		3.57		0.92		1.70
Net Removal[2]	0.12	71	1.52	67	2.53	38	0.83	14	1.45
Litter	0.05	29	0.75	23	4.07	62	5.89	86	-
Total	0.17		2.27		6.60		6.72		
Control Aspen									
Precipitation	0.42		0.37		1.36		0.27		0.34
Net Precipitation	0.30		3.62		3.85		0.60		0.89
Net Removal	-0.12		3.25	26	2.49	6	0.33	1	0.55
Litter	0.30	100	9.06	74	40.39	14	29.13	99	-
Total	0.30		12.31		42.88		29.46		
Control Spruce									
Precipitation	0.41		0.38		1.31		0.21		0.55
Net Precipitation	0.30		2.93		2.29		0.53		2.08
Net Removal	-0.11		2.55	66	0.98	13	0.32	6	1.53
Litter	0.07	100	1.32	23	6.39	87	5.08	94	-
Total	0.07		3.87		7.37		5.40		

[1] Net Precipitation = Throughfall + Stemflow

[2] Net Removal (Nutrients removed from the forest canopy) is equal to the amounts of nutrients in net precipitation loss the amounts of nutrients in incident precipitation

More than twice the total amount of potassium recycled from black spruce trees to the forest floor was in throughfall and stemflow (60%) compared to litterfall (23%). As for trembling aspen, sodium was removed from precipitation by the black spruce canopy.

5.1.6 Magnitude of the Chemical Components of Throughfall

The nutrient content of throughfall is largely a function of nutrient input by incident precipitation, leaching potential of the incident precipitation, the physiological condition of the leaf and the chemical form of the element in the leaf (Eaton et al. 1973). The washing of impacted particulates from leaves may also be important in determining throughfall nutrient content (McColl and Bush 1978). The amounts of nutrients in throughfall were highly correlated with the amount of incident precipitation (Figure 4). For each species the amounts of each element removed from the tree canopy was highly correlated ($r^2>0.8$) with the amount of precipitation. Reiners (1972) and Carlilse et al. (1967) also found similar relationships.

A comparison of the amounts of nutrients leached from tree canopies of a number of species reveals several interesting points (Table 18). In general, potassium is the most easily leached element from tree crowns of both hardwoods and softwoods. The general pattern of enrichment of bases is K > Ca > Mg. High values for sodium were

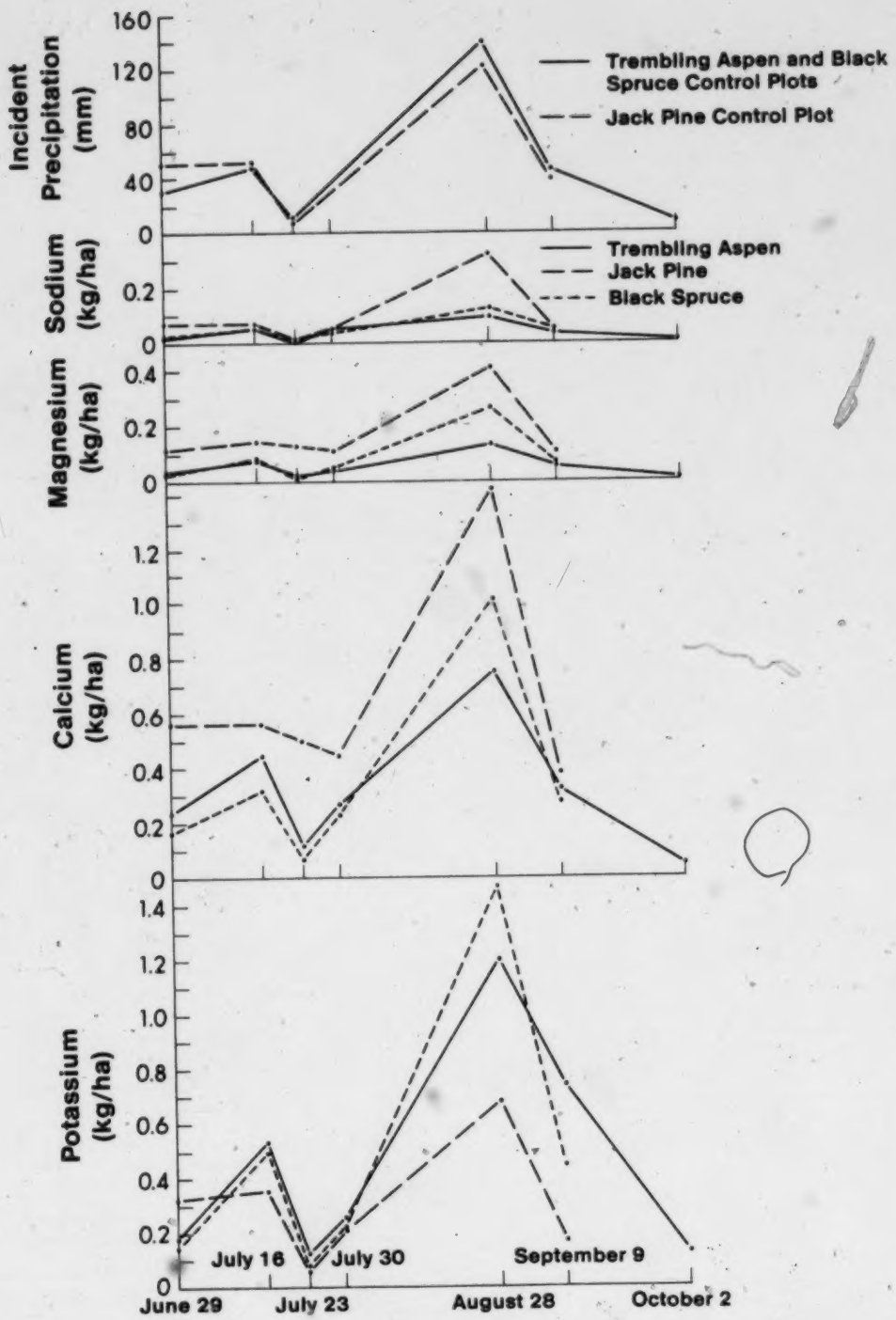


Figure 4 Incident precipitation and deposition of nutrients via throughfall in the three forest types (control site) from June through to October 1976.

Table 18. Annual removal of nutrients from tree crowns by rain in this and comparable studies elsewhere in the world.

Species	Locality	Distance from Coast (km)	Annual Rainfall (cm)	Annual Removal (kg/ha) Na	K	Ca	Mg	SO4=-S	Source
P. tremuloides[1,2]	Alberta, Canada	1920	33	-0.1	3.3	2.5	0.3	0.6	Present study
P. tremula[2]	Voronezh, USSR	800			2.0	5.1	0.9		Sviridova
Oak[2]	Voronezh, USSR	1920			3.3	6.0	1.2		(1960)
Q. petreae	Lancashire, Eng.	8	171	20.2	25.2	9.9	4.7		Carlisle et al. (1966)
Hardwoods	S.E. England	27	81	11.8	25.0	13.8	7.0		Magdwick and Ovington (1959)
Nothofagus truncata	New Zealand	16	135	11.2	24.4	6.0	2.2		Miller (1963)
P. sylvatica[1,2]	South Sweden		95	10.0	11.2	6.6	2.5	10.6	Nihlgard (1970)
Hardwoods[1]	N.C., USA		117		17.2	11.1	3.3		Wells et al. (1972)
P. banksiana[1,2]	Alberta, Canada	1920	30	0.1	1.5	2.5	0.8	1.5	Present study.
P. banksiana[1]	Ontario, Canada		95		7.6	1.6	0.4		Foster (1974)
Pines	E Tennessee, USA		76		18.7	17.4	2.8		Henderson et al. (1977)
P. taeda[3]	N.C., USA		117		8.7	6.4	1.7		Wells et al. (1972)
Pine[2]	Voronezh, USSR	800			1.0	6.0	0.9		Sviridova (1960)
Softwoods	S.E. England	27	81	14.5	19.8	13.4	5.0		Magdwick and Ovington (1959)
P. mariana[1,2]	Alberta, Canada	1920	33	-0.1	2.6	1.0	0.3	1.5	Present study
Pseudotsuga taxifolia	New Zealand	81	170	-1.8	18.5	2.0			Will (1959)
P. abies[1,2]	South Sweden		95	20.6	25.2	13.9	5.2	46.3	Nihlgard (1970)
Pseudotsuga menziesii	Oregon, USA		240		21.6	2.3	0.9		Abee and Lavender (1972)

[1] includes stemflow
[2] growing season only
[3] includes contribution from hardwood understory

recorded at sites close to the ocean. The high values of sulphate sulphur reported for European beech (Fagus sylvatica) and Norway spruce (Picea abies) by Nihlgard (1970) were attributed to atmospheric pollution.

5.1.7 Seasonal Changes in Chemical Components of Throughfall

A number of investigators have observed seasonal variation in the removal of material from the forest canopy by precipitation (Will 1959, Voigt 1960, Eaton et al. 1972). In this study seasonal trends were not clear because of the strong influence of the amount of incident precipitation on throughfall nutrient content. For pine and spruce the quantities of sodium and magnesium in throughfall generally followed the pattern of precipitation (Figure 4). The amounts of calcium and magnesium were closely related to amounts of precipitation early in the summer but declined somewhat unexpectadly on the September 9 sample date. This may be because the prior heavy storm (>12.0 cm in 36 hours) caused a depletion in the nutrient content of the leaves. The subsequent shower occurred before normal levels had built up again, resulting in lower than expected throughfall concentrations of calcium and magnesium.

This effect was not observed for aspen (Figure 4) and could possibly reflect a higher transpiration rate for aspen and a faster build up in leaf nutrient content. Zamierowski

and McCloskey (1975) noted marked differences between species in the time for replacement of nutrients lost by leaching. It is interesting to note the differences in the nutrient concentrations in aspen throughfall on the October 2 sample date. On this sample date the throughfall collectors contained a large amount of leaf litter and the throughfall data reflect the relative leachability of the various elements from the leaf litter. The concentration of potassium was particularly high whereas calcium was not unusually high (Appendix 10.3). This is consistent with the observation of Gosz et al. (1972) that much of the potassium in litter is released by the physical process of leaching by rainwater, whereas calcium, which is a structural component of cells, depends upon decomposition and biological release. The high concentration of potassium on September 9 perhaps represents the maximum for potassium after leaf abscission noted by other researchers (Denaeyer - DeSmet 1966, Eaton et al. 1973, Gosz et al. 1975).

5.2 DISCUSSION

Leaching of nutrients from tree crowns of each species was highly correlated with the amount of net precipitation. Distribution of recycled nutrients in stemflow and throughfall both temporally and spatially is therefore closely related to the distribution and amount of incident precipitation. The recycling of nutrients in throughfall and stemflow must occur, therefore, at uneven intervals

throughout the growing season.

Throughfall contained lower concentrations of nutrients than stemflow but total nutrient returns were much greater in throughfall because of the larger volume of water that reaches the soil as throughfall. Of the three species studied, jack pine returned the greatest amount of sodium and magnesium in throughfall and stemflow, trembling aspen the greatest amount of potassium and calcium, and black spruce the greatest amount of sulphate sulphur. In total, throughfall from trembling aspen contained the largest quantities of soluble nutrients while throughfall from jack pine and black spruce contained about equivalent lesser amounts.

Stemflow, compared to throughfall, was of minor importance in the addition and return of nutrients to the forest floor when considered on an area basis. However, aspen stemflow was as important as throughfall in the addition of calcium. Significant amounts of sodium and potassium were also added to the forest floor in aspen stemflow. The addition of nutrients in stemflow increases the heterogeneity of nutrient additions by producing areas with high quantities of elements close to the tree stems. Stemflow has great importance when only its zone of direct influence is considered. Voigt (1960) has shown that stemflow is concentrated near the base of the trunk and Gersper (1970) reported that the greatest influence of beech

stemflow in concentrating fallout radioisotopes is limited to a sphere of influence extending 30 cm from the trunk and to a depth of 30 to 45 cm. By using a mean stem diameter of 19.0 cm for control site aspen and a sphere of influence extending 30 cm from the trunk, the amount of stemflow received over this area amounted to about 8 times the incident rainfall received over a similar area in the open. On average this area received six times as much calcium, 86 times as much magnesium and 28 times as much sulphate sulphur as an equal area in the open. These values are minimum values because on several occassions the stemflow volumes were underestimated because the collection vessels overflowed.

Stemflow in aspen may facilitate rapid recycling of soluble nutrients (particularly K, Ca, Mg) since stemflow water is available quickly to absorptive roots at the base of the tree (Voigt 1960). Stemflow water may also have a considerable impact on the physical and chemical properties of soils. Patterson (1975) and Mina (1967) found that trends in surface-soil pH were correlated with the pH of stemflow and throughfall of each tree species. Stemflow and throughfall provide a means of transfer of soluble nutrients from the living biomass component of an ecosystem to the available nutrient component and thus form an integral part of the intrasystem nutrient cycle (Figure 5). The content of this nutrient pool is dependent on the relative leachability of each element. The amounts of nutrients recycled in

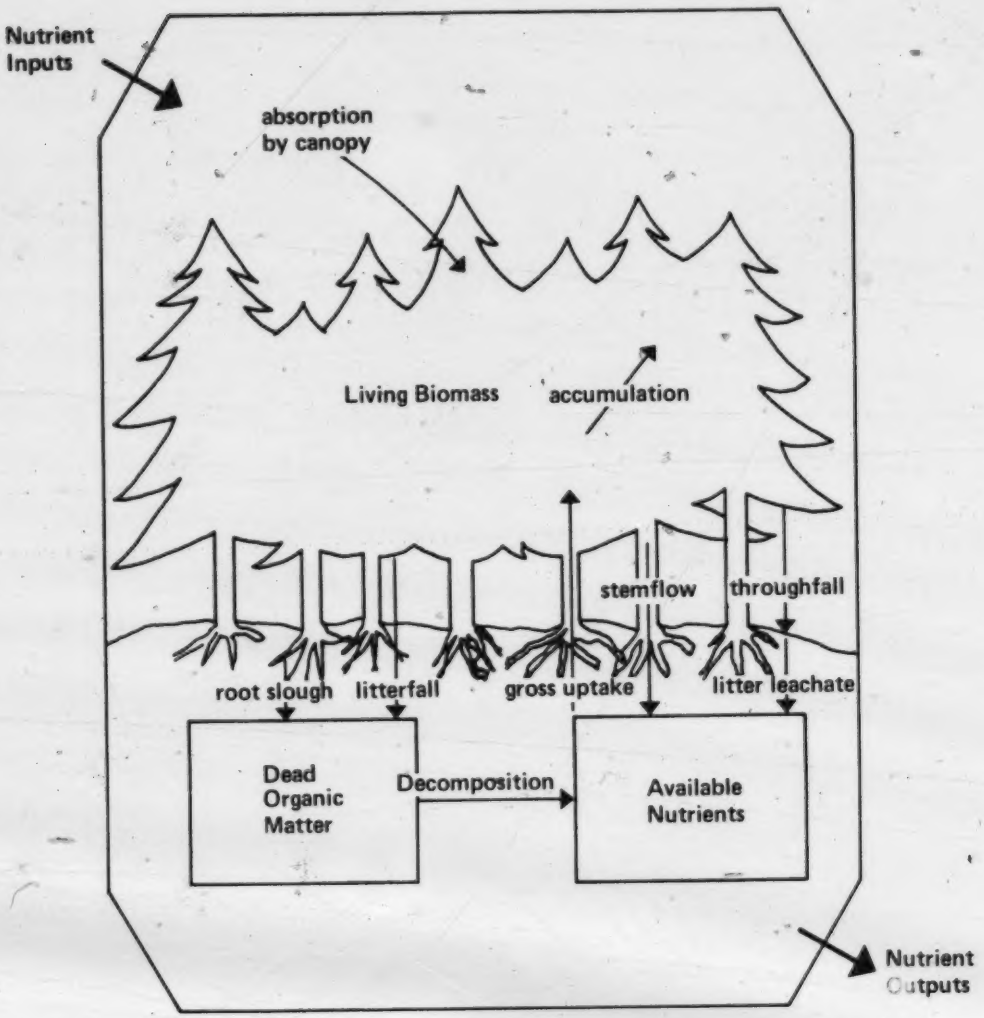


Figure 5 Components of the nutrient cycle for a forest ecosystem showing sites of nutrient accumulation and major pathways. Nutrient inputs include weathering of minerals, and nutrients in rain, snow and particulate matter. Nutrient outputs include losses with drainage waters and formation of secondary minerals. (After Eaton et al. 1973)

throughfall and stemflow were shown, in general, to be less than the amounts recycled in litterfall for all tree species studied. However, nutrients in throughfall and stemflow are added directly to the available nutrient pool without the need of any decomposition process on the forest floor (Figure 5). Throughfall and stemflow, therefore, take on added significance in mineral cycling in boreal forest ecosystems where decomposition of litter is slow.

The leaching of nutrients and subsequent reabsorption of the leachates by the same plant can be an important function in the mineral nutrition of that plant. This is particularly so for the elements calcium and magnesium which once absorbed by the leaves, do not move basipetally from the leaves and are not translocated to areas of new growth (Bukovac and Wittwer 1957). Throughfall and stemflow provide a means of redistributing basipetally immobile nutrients from mature tissues to young rapidly metabolising tissues. It is also interesting to note that mature leaves are generally more susceptibile to leaching than young growing leaves thus preserving the integrity of this pathway. Considerable quantities of calcium and magnesium were recycled in this manner in jack pine and black spruce and a lesser amount of calcium in trembling aspen.

Foliar absorption of nutrients has been demonstrated by a number of researchers (Ingham 1950, Tukey and Wittwer 1958, Will 1959, Carlilse et al. 1966). Witherspoon (1964)

found that understory plants absorbed radio-cesium from white oak throughfall directly through their foliage. This could result in even more rapid turnover of nutrients in forest ecosystems. It has also been hypothesized that not only are some plants adapted to an environment by virtue of the nutrients removed from their foliage but some plants may be adapted to an environment in which their nutrients are supplied in the leachate from other plants (Tukey and Mecklenburg 1964). Indeed Tamm (1950) showed that mosses may gain a considerable portion of their nutrients from the throughfall of overhead conifers and epiphytic lichens were found to absorb ammonium and nitrate from solutions flowing over their surfaces. (Lang et al. 1976). It has been suggested that some species of epiphytes may grow in association with certain tree species in part because of the nutrients which they receive from their hosts (Stenlid 1958). Plant leachates have also been shown to suppress the growth of other plant species, particularly in desert plants (Rice 1974). Throughfall and stemflow from forest trees may, therefore, be factors which influence the distribution and association of plants.

6. IMPACT OF SULPHUR DIOXIDE ON THROUGHFALL AND STEMFLOW CHEMISTRY

6.1 RESULTS

6.1.1 Acidity and Nutrient Contact of Throughfall and Stemflow

The mean nutrient concentrations and pH of rain for the two sites are given in Table 19. Complete data are presented in Appendix 10.3. The mean nutrient concentrations presented are geometric means where each concentration value is weighted according to the sample volume. The mean sulphate sulphur concentration in rain at the exposed site was nearly twice as great as the concentration in rain at the control site.

A t-test indicated that the mean volume, nutrient concentrations and mean pH of rain at the exposed site were not significantly ($p<0.05$) different from rain at the control site. On average, rain was not acidic at either site. The exposed plots received on average more than twice the amount of sulphur dioxide than the control sites as indicated by the sulphation discs (Table 20).

Mean nutrient concentrations and pH of throughfall and stemflow at both sites are given in Table 21. Note that these figures represent the mean values from 5-10 sample periods with each experimental plot at each sample date,

Table 19. Mean[1] nutrient concentrations (ppm) and mean[1] pH[1] of incident rain collected during the summer of 1976 at the two sites of the nutrient cycling study.

	Site			
	Control		Exposed	
	Mean	SD[2]	Mean	SD
Na^+	0.14	0.09	0.15	0.12
K^+	0.17	0.18	0.17	0.13
Ca^{++}	0.44	0.10	0.45	0.15
Mg^{++}	0.08	0.05	0.06	0.03
$SO_4^{=}$-S	0.16	0.10	0.31	0.21
pH	5.73		5.72	

[1] Geometric means weighted by the sample volumes
[2] Standard deviation

Table 20. Mean total sulphation for the control site and the exposed site of the nutrient cycling study. Values are expressed as mg SO_3 equivalent/100 cm^2 sulphation disc area/day.

Control Site	Exposed Site
0.023	0.053

Table 21. Mean[1] nutrient concentrations (ppm) and mean[1] pH of throughfall and stemflow collected during the summer of 1976

	Species											
	Trembling Aspen				Jack Pine				Black Spruce			
	Control		Exposed		Control		Exposed		Control		Exposed	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Throughfall												
Na^+	0.12	0.04	0.12	0.03	0.18	0.04	0.19	0.12	0.13	0.02	0.17	0.05
K^+	1.43	0.68	3.76	6.24	0.71	0.22	1.78	0.88	1.00	0.22	1.09	0.65
Ca^{++}	0.97	0.31	3.08	3.24	1.30	0.24	1.82	1.49	0.81	0.15	1.41	1.12
Mg^{++}	0.16	0.05	0.57	0.97	0.32	0.05	0.47	0.57	0.18	0.04	0.20	0.08
$SO_4^{=}$-S	0.39	0.21	0.42	0.18	0.75	0.39	1.54	1.48	0.68	0.24	0.77	0.32
pH	6.14		6.49		5.09		4.78		5.03		5.14	
Volume (ml)	1164	1173	1243	891	1279	1438	1165	988	1210	1370	1173	1213
Stemflow												
Na^+	0.12	0.02	0.14	0.04	0.48	0.15	0.65	0.33	0.90	0.79	0.84	0.61
K^+	2.53	0.44	4.29	1.53	1.91	0.57	8.48	3.87	6.32	1.84	5.34	2.35
Ca^{++}	8.84	3.13	16.87	7.13	9.41	5.18	11.76	8.94	10.66	2.83	11.10	11.19
Mg^{++}	1.22	0.46	2.08	1.26	1.70	1.19	3.08	1.94	1.91	0.99	1.41	0.53
$SO_4^{=}$-S	0.62	0.39	2.25	0.96	4.84	3.45	15.88	10.27	5.59	4.71	6.92	1.82
pH	7.55		7.82		4.58		3.48		4.23		4.19	
Volume (ml)	>11357	8198	>11850	6115	2802	4560	5097	7968	676	1471	815	1456

[1] Geometric means weighted by the sample volumes
[2] Standard deviation

providing approximately 20 throughfall and 10 stemflow samples. The total amounts of nutrients returned to the forest floor in throughfall and stemflow at both sites are given in Appendix 10.3.

Assuming that the chemical composition of the rain at each site was the same (except for SO4=-S) it can be seen that larger quantities of the cations K+, Ca++ and Mg++ were being removed from the canopies of trembling aspen and jack pine at the site exposed to sulphur dioxide pollution (Table 21). For aspen throughfall there was a greater concentration of Ca++, Mg++ and SO4=-S at the exposed site than the control site even though the mean sample volume was slightly higher at the exposed site. This greater nutrient concentration was associated with a higher throughfall pH at the exposed site. Aspen stemflow at the exposed site tended to have higher K+, Ca++, Mg++ and SO4=-S concentrations and higher pH despite the higher average volume at the exposed site compared to the control site. The concentrations of K+, Ca++, Mg++ and SO4=-S in jack pine throughfall were higher at the exposed site than at the control site. The pH of the exposed site throughfall was, however, lower. Jack pine stemflow, like throughfall, had higher concentrations of K+, Ca++, Mg++ and SO4=-S at the exposed site than the control site. The pH of exposed pine stemflow was also markedly lower than for the control site. The differences between the exposed spruce site and control site were not as evident as for the other species. Only the Ca++ concentration in

throughfall was greater at the exposed site. The differences may have been masked by the greater differences in the size of the trees on the two spruce plots (Table 1). The exposed plot trees were smaller on average and had a less dense canopy than the control plot trees. Rain at the exposed plot would have washed over less foliage than rain at the control site. Therefore, the resultant greater leaching at the control site could have prevented any increased leaching, caused by sulphur emissions at the exposed site, from becoming apparent.

The concentration of Na^+ was similar in the throughfall of all three species at both sites. Throughfall Na^+ concentration was also about equal to the average concentration in incident precipitation at both sites. Sodium, therefore, is only leached from jack pine or black spruce to a small extent. Since the concentration of sodium in trembling aspen throughfall is slightly less than in the incident precipitation, and because throughfall volume is less than incident precipitation, sodium must be absorbed by the aspen canopy. This is also shown in Appendix 10.3 where on several occasions the amount of sodium in rain is less than the total amount of sodium in throughfall plus stemflow.

The similarity in concentrations of sodium between the control and exposed sites suggests that sulphur dioxide emissions at the exposed site are not influencing the

leaching of sodium from the tree crowns. This is consistent with the findings of Wood and Bormann (1975). They found that an acidified artificial mist increased the leaching of K^+, Ca^{++}, and Mg^{++} from sugar maple (Acer saccharum) seedlings but the leaching of Na^+ remained the same or decreased slightly.

Table 22 shows the weighted mean nutrient concentration and weighted mean pH for jack pine and trembling aspen throughfall and stemflow for a given sample period when the amount of precipitation at each site was similar. A similar comparison was not possible for black spruce because there was not a sample period when the amount of precipitation at each plot was similar. The concentrations of nutrients at the exposed site were generally higher than at the control site for both species. The differences which were statistically significant ($p<0.05$, Student's t-test) are indicated. Aspen throughfall and stemflow had a higher pH at the exposed site whereas jack pine throughfall and stemflow were lower in pH at the exposed site.

6.1.2 Source of nutrients in throughfall and stemflow

Since nutrient quantities in dry fallout were not determined separately, these quantities are included in the amounts of nutrients recorded in the throughfall and stemflow. A number of researchers have recognized the possibility that aerosols and dust may adhere to leaves,

Table 22. Mean nutrient concentrations and pH of rain; and of trembling aspen and jack pine throughfall and stemflow. Values are from a single sample period. The mean value of a given variable (Na^+, K^+ etc.) at the control site was compared to the corresponding mean value at the exposed site according to Student's t-test. Pairs of values which are significantly different ($p<0.05$) are indicated by asterisks beside the exposed site values.

	Trembling Aspen		Jack Pine	
	Control	Exposed	Control	Exposed
Precipitation (mm)	45.0	43.0	45.4	41.6
Throughfall				
Na^+	0.19	0.10	0.19	0.24
K^+	0.86	1.03	0.99	2.26*
Ca^{++}	0.88	1.48*	1.49	1.77
Mg^{++}	0.13	0.18*	0.39	0.57
$SO4^{=}$-S	0.16	0.49*	1.09	1.78
pH	6.03	6.41*	5.04	4.72*
Volume (ml)	1037	1266*	1344	1055*
Stemflow				
Na^+	0.15	0.19	0.73	0.91
K^+	2.83	4.51*	2.82	11.79
Ca^{++}	11.69	26.37*	18.31	28.76
Mg^{++}	1.64	3.89*	2.59	5.75*
$SO4^{=}$-S	0.52	4.21*	12.87	33.00*
pH	7.56	8.03*	4.99	3.50*
Volume (ml)	16025	11138	1266	2544
Rain				
Na^+	0.10	0.09	0.09	0.23
K^+	0.07	0.10	0.10	0.21
Ca^{++}	0.47	0.49	0.21	0.44
Mg^{++}	0.08	0.06	0.02	0.04
$SO4^{=}$-S	0.08	0.10	0.19	0.60
pH	5.65	5.03	5.82	5.30

branches and stems and then add significantly to the chemical concentration of throughfall and stemflow (Eriksson 1955, Tamm and Troedsson 1955, Hart and Parent 1974). Nihlgard (1970) found in Scania, South Sweden (in a region subject to air pollution in the form of acid rain and acid particulates) that hydrogen ions, potassium and manganese in spruce throughfall resulted largely from leaching. Magnesium, sodium, calcium and chloride, on the other hand, could have been derived to a large extent from aerosols.

In a recent study of atmospheric particulate deposition in the oil sands area Barrie (1978) found that in a region northwest of the emission source the main source of calcium and magnesium was from wind blown dust. The lowest deposition rates for those elements with a strong wind blown dust component was found to occur at Muskeg Mountain 38 km to the east. He also found that particulate sulphur was largely of anthropogenic origin even at the site subject to wind blown dust (11 km NW of the emission source). The exposed site for this study was located 32 km SE of the emission source well away from the previously mentioned sources of wind blown dust and would be expected to be similar to the situation found at Muskeg Mountain. Particulate deposition from the emission source could, therefore, be an important component of the nutrient content of throughfall and stemflow at this site, particularly for sulphate sulphur. This component represents the filtering action of the forest canopy on airborne particulates and

aerosols.

Mayer and Ulrich (1976) proposed an indirect method to separate this component from the nutrients removed from the tree leaves by leaching. They assumed that during the leafless winter period, leaching of nutrients from the trees is very small and therefore any nutrients added to the incident rain in throughfall must be derived from particulates deposited on the tree. Unfortunately such an approximation is not possible for this study.

Another method to determine the contribution of particulate matter to the nutrient content of throughfall is to determine the relative behaviour of the nutrient ions with respect to the forest canopy (Attiwill 1966). Tables 23 and 24 show the ratios of concentrations (in meq/l) of the ions in rain, and in aspen and jack pine throughfall. The increase of an ion (calcium) relative to the other ions is expressed as a ratio:

$$\text{Increase} = \frac{\text{Increase in } Ca^{++} \text{ concentration due to forest canopy}}{\text{Increases in } K^{+}, Mg^{++}, Na^{+} \text{ or } SO_4^{=}\text{-S concentrations due to forest canopy.}}$$

where the increase in concentration of each ion is calculated as:

$$C2 - \frac{V1C1}{V2}$$

where C1 is the ionic concentrations in volume V1 of rainwater at the open plot, and C2 is the concentration in

Table 23. Increases in the ratio of ions relative to calcium due to the forest canopy of trembling aspen. Ratios were calculated from the concentrations in meq/l (After Attiwill 1966).

Date	Ca++/Na+			Ca++/K+			Ca++/Mg++			Ca++/SO4=-S		
	o[1]	uc[2]	i[3]	o	uc	i	o	uc	i	o	uc	i
Control Site												
29 June	5.45	11.72	-92.70	6.74	2.54	0.81	11.53	4.62	4.82	1.22	1.43	2.16
16 July	4.59	9.52	51.50	3.39	1.66	0.61	4.05	3.70	5.70	1.68	1.60	1.92
23 July	2.16	15.24	-2.02	2.23	1.82	0.76	3.88	3.61	5.48	2.84	1.87	1.64
30 July	5.40	5.46	5.01	13.10	2.02	0.24	1.58	4.25	-1.28	4.70	4.57	5.19
27 Aug.	3.06	9.08	-1.76	11.15	1.22	0.18	3.04	3.15	5.80	-	2.62	0.86
9 Sept.	4.02	9.65	-8.53	11.71	0.85	0.19	4.25	3.49	4.60	1.34	2.46	-17.82
2 Oct.	4.13	8.09	-64.51	8.78	0.71	0.18	5.46	3.23	3.62	-	-	-
Mean	4.12	9.82		8.16	1.55	0.42	4.83	3.72	4.47	2.35	2.43	4.93
Exposed Site												
30 June	2.16	12.92	-2.16	3.30	2.11	0.74	4.45	4.19	6.42	1.23	1.44	2.31
15 July	2.20	16.33	-3.36	4.09	1.86	0.66	6.68	4.47	5.81	0.59	3.44	-1.46
29 July	6.25	17.47	-76.15	9.56	2.82	0.98	4.96	4.97	8.19	3.92	2.39	2.37
10 Aug.*	-	14.24	-	-	2.21	-	-	3.76	-	4.97	-	-
25 Aug.	0.82	13.95	29.84	0.51	1.55	0.86	0.38	3.87	9.68	0.27	3.58	8.31
8 Sept.	3.83	56.76	481.39	13.01	6.32	3.13	6.07	16.98	31.67	0.57	9.50	-485.60
10 Oct.	5.36	81.12	269.64	10.24	1.10	0.54	3.10	2.21	3.59	-	-	-
Mean	3.44	30.40		6.79	2.57	1.15	4.29	5.78	10.89	2.25	4.91	

[1] Value for incident rain
[2] Value for throughfall
[3] $i = \frac{\text{Increase in Ca++ concentration due to canopy}}{\text{Increases in Na+, K+, Mg++ and SO4=-S concentrations due to canopy}}$

Table 24. Increases in the ratio of ions relative to calcium due to the forest canopy of jack pine. Ratios were calculated from the concentrations in meq/l (After Attiwill 1966).

Date	Ca++/Na+			Ca++/K+			Ca++/Mg++			Ca++/SO4=-S		
	o[1]	uc[2]	i[3]	o	uc	i	o	uc	i	o	uc	i
Control Site												
29 June	6.63	8.82	10.34	12.68	3.41	1.11	5.26	2.97	3.65	1.66	1.35	1.47
16 July	2.68	9.21	15.97	4.10	3.06	1.49	2.37	2.38	3.48	0.88	1.08	1.42
23 July	5.65	8.26	16.42	12.49	3.14	0.84	4.86	2.69	2.87	1.83	0.94	0.74
30 July	6.31	9.52	10.72	17.17	4.07	1.56	6.68	2.44	3.13	3.52	2.10	2.22
27 Aug.	1.41	5.06	163.57	4.46	4.11	2.05	9.71	2.08	2.64	-	2.25	2.04
9 Sept.	3.90	9.11	31.89	9.48	4.45	1.75	5.16	2.24	2.79	-	2.06	1.65
2 Oct.	3.25	-	-	11.06	-	-	3.44	-	-	-	-	-
Mean	4.43	8.83	38.04	10.06	3.71	1.47	6.34	2.47	3.09	1.97	1.37	1.46
Exposed Site												
30 June	2.16	11.79	-21.14	3.30	2.88	1.41	4.45	1.61	2.19	1.23	0.82	0.92
15 July	2.20	7.82	-7.62	4.09	1.54	0.54	6.68	2.15	2.36	0.59	0.88	1.75
29 July	6.25	8.76	21.60	9.56	1.39	0.30	4.96	2.50	2.29	3.92	0.82	0.45
10 Aug.	-	23.11	-	-	4.03	-	-	5.24	-	-	2.80	-
25 Aug.	8.20	10.77	15.27	5.13	1.85	0.53	3.79	2.67	3.22	2.67	1.06	0.76
8 Sept.	3.83	5.33	10.19	13.01	1.63	0.38	6.07	3.15	3.12	0.57	0.67	1.08
10 Oct.	5.36	7.61	12.33	10.24	0.62	0.16	3.19	2.84	4.18	-	-	-
Mean	4.67	8.68		7.56	1.65	0.55	4.86	2.49	2.89	1.80	0.85	0.99

[1] Value for incident rain
[2] Value for throughfall
[3] $i = \frac{\text{Increase in Ca++ concentration due to canopy}}{\text{Increases in Na+, K+, Mg++ and SO4=-S concentrations due to canopy}}$

volume V2 under the canopy. The calculation of the increase in concentrations from incident rain to throughfall therefore allows for the lower volume of throughfall compared to incident rain.

The ratio of the ions was chosen to be relative to calcium because it was the predominant cation in the incident precipitation. It is not important that it is not inert with respect to the canopy since what is of interest is the behaviour of the ions relative to one another and with respect to the canopy at each site.

Clearly the canopy has altered the chemical composition of the rainwater with a decrease in the ionic ratios (except Ca/Na). The negative relative increase in sodium with respect to calcium for aspen and on some occasions exposed pine confirms the earlier suggestion that sodium in the rain is being absorbed by the tree crown (see also Appendix 10.3). Best and Monk (1975) also showed that throughfall sodium in a hardwood forest and an eastern white pine forest was less than the sodium in the incident rain. The negative value for the increase of Ca/SO4= for control aspen on September 9 (Table 23) and exposed aspen on September 8 (Table 24) indicates that throughfall SO4=-S was less than incident rain SO4=-S. However the total of throughfall and stemflow SO4=-S exceeded the rain SO4=-S content (Appendix 10.3). The negative value for exposed aspen on July 15 (Table 24) may have resulted from an analytical error

causing an overestimation of the amount of SO4=-S in the incident rain.

Since the open rain collectors were left uncovered between collection periods it would be expected that they would receive deposits of aerosols as would the trees. If the chemical composition of aerosols removed by washout in the incident rain was the same as those impacting on the tree canopies and there was no interaction between the tree canopy and the aerosols to change the aerosol chemical composition, then it would be expected that the ionic ratios in incident rain and throughfall would be about the same. That is, no element would become enriched relative to the others. Moreover, the ratio of ions under the canopy of jack pine and aspen would be similar if only soluble particulates were being removed from the trees. The observed increase in the concentration of ions relative to calcium as rain passes through the canopy suggests that the ions are being removed from the leaves by leaching or there has been an exchange between the aerosol elements and elements in the leaf with subsequent removal by rain. For example, the average calcium : potassium ratio decreased from 8.16 in the open to 1.55 under the aspen canopy at the control site (table 23). The cause of this lower ratio was the greater amount of potassium than calcium which was removed from the tree crowns by leaching.

By referring to the increase in the ratios with respect

to the canopy the order of removal of the nutrients from the canopy can be determined. For example for pine throughfall at the control site the ratio:

$$\frac{\text{increase in Ca concentration due to forest canopy}}{\text{increase in K concentration due to forest canopy}} \quad 1$$

and therefore calcium is more readily leached than potassium. For the exposed site the same ratio is less than one suggesting potassium is more readily leached than calcium. By calculating the various combinations of ratios one is able to determine the relative removal of the various nutrients at each site (Appendix 10.6). For control and exposed aspen this order was:

K > Ca > SO4=-S > Mg > Na

For control pine the order was:

Ca > K > SO4=-S > Mg > Na

while for exposed pine the order became:

K > Ca > SO4=-S > Mg > Na

At the exposed pine site the Ca/SO4=-S ratio was at times greater than one and at other times less than one (Table 24). This may be because of a fluctuating deposition of sulphur from the emission source due to changing wind patterns.

Several researchers (Eaton et al. 1972, Henderson et al. 1977) have used the ratio of the net amount of each element removed from the forest canopy to the standing crop of each element to indicate the relative leachability of different nutrient elements. However, this has the

disadvantage of a changing standing crop of each element throughout the growing season (Guha and Mitchell 1966) and the poor relationship between the amount of each element leached and its concentrations in the leaf.

6.1.3 Determination of the Factors Influencing Throughfall Chemistry

Mecklenburg et al. (1966) suggested that the mechanism of cation loss by leaching is:

1) by exchange of cations on the cuticle and cell wall exchange sites (-OH and -COOH groups of cellulose, hemicellulose, phospholipid and polyuronide molecules) with hydrogen ions from the leaching solutions;
2) by diffusion of ions from the translocation stream within the foliage into the leaching solution; or
3) a combination of both exchange and diffusion.

The process of cation exchange appears to be in part responsible for the leaching of cations from trembling aspen. For both sites, hydrogen ions were removed as rain passed through the canopy and there was an accompanied increase in the cation content of the rain (Table 25). For the control site hydrogen ions made up 38% of the total cations in the incident rain and only 20% of the total cations in the throughfall. A greater change was seen at the exposed site where hydrogen ions comprised 44% of the total

Table 25. Cation and sulphate sulphur flux for trembling aspen and jack pine for the control and exposed sites of the nutrient cycling study, 1976.

	Precipitation (mm)	Total Cations (Na^{++}, K^{+}, Ca^{++}, Mg^{++}) (eq/ha)	$SO_4^{=}$-S (eq/ha)	H^{+1} (eq/ha)	H^{+} as Fraction of Total Cations (%)
		Control Aspen			
Rain	318	116	21	70	38
Throughfall	265	226	49	57	20
Stemflow	19	113	6	0	
Net		223	34	-13	
		Exposed Aspen			
Rain	258	68	46	54	
Throughfall	220	384	54	34	8
Stemflow	18	198	23	0	
Net		515	31	-20	
		Control Pine			
Rain	289	68	16	64	48
Throughfall	289[2]	319	103	144	31
Stemflow	2	7	3	4	
Net		258	90	84	
		Exposed Pine			
Rain	258	74	46	54	42
Throughfall	200	247	134	210	46
Stemflow	1	5	5	22	
Net		178	93	178	

[1] Free acidity calculated from the pH values
[2] Throughfall exceeded incident precipitaiton on several occasions (See Appendix 8.3).

cations in incident rain and only 8% of the total cations of in throughfall. There was a greater amount of cations in the throughfall and stemflow of the exposed aspen than the control aspen even though the volume of water was much less.

For control pine there was an increase in the amount of hydrogen ions from rain to throughfall associated with the increase in cations. The percentage of hydrogen ions to the total cations decreased, however, from rain to throughfall (Table 25). This is opposite to the situation for aspen where an increase in the pH of rain to throughfall was observed. This does not necessarily contradict the hypothesis of cation exchange, however, as the additional acid in jack pine throughfall may be due to the presence of organic acids. A large number of organic acids have been shown to be leached from various plants (Morgan and Tukey 1964). At the exposed jack pine site there was an increase in the amount of acid in throughfall with an increase in the hydrogen ions as a percentage of the total cations. There was also a marked increase in the amount of sulphur deposited in throughfall at the exposed site in comparison to the control site even though the throughfall volume was less at the exposed site.

6.1.4 Principal Component Analysis of Throughfall and Stemflow Data

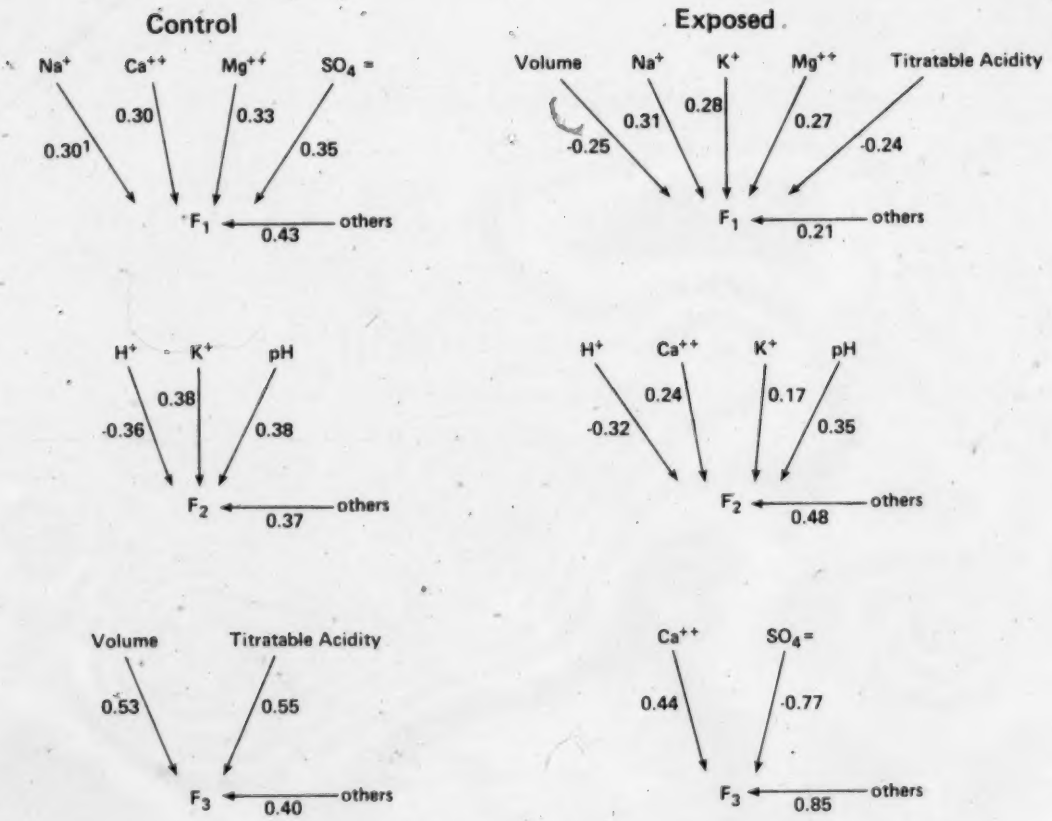
This section concerns the results of principal

component analyses of the throughfall and stemflow data. The rationale for such analyses is given in Section 3.4 and details of the procedure are given in Appendix 10.4.

6.1.4.1 Aspen throughfall. Principal component analysis of the data showed that for both the control site and the exposed site three factors determined most of the variance in the data (Figure 6). For the control site, factor one (F1) is highly correlated with Na+, Ca++, Mg++ and SO4=-S concentrations. Factor two (F2) is negatively correlated with H+ but positively correlated with K+ and factor three (F3) is correlated with the volume and titratable acidity. I will call F1 the "leaching factor", F2 the "acidity factor" and F3 the "volume factor".

For the exposed site the leaching factor and volume factor appear to be combined while the acidity factor is correlated with both Ca++ and K+. Factor three at the exposed site is related to both Ca++ and SO4=-S. concentrations.

In terms of the hypothesis of cation exchange, factor one at the control site is due to the normal leaching of Na+, Ca++, Mg++ and SO4=-S. Factor two is related to the natural pH of aspen throughfall. This pH is derived from an exchange of hydrogen ions in the canopy as rain passes through the canopy. Since K+ is the ion in greatest concentration in the throughfall (the most readily leached)



[1] Factor score coefficient

Figure 6 Simplified Path diagrams showing the relationship between the principal components and variables for Aspen (*Populus tremuloides* Michx.) throughfall at a control site and a site exposed to sulphur dioxide.

it would have been replaced most frequently by hydrogen ions in the rain. At the control site the K^+ concentration is positively correlated with F2 while H^+ is negatively correlated with F2 (Figure 6) and K^+ is negatively correlated with H^+ (Appendix 10.4). Therefore K^+ is inversely related to H^+ as was reasoned above. Factor three is considered a volume factor since the titratable acidity is a measure of total acidity and is more directly related to volume than to pH which is a logarithmic function of acid concentration. For the exposed site the "leaching factor" and "volume factor" appear to be combined. The volume and titratable acidity variables are negatively correlated with F1 whereas Na^+, K^+ and Mg^{++} concentrations are positively correlated with F1. This factor could, therefore, represent the volume dependent leaching factor. Factor two is correlated with both calcium and potassium concentrations and negatively correlated with H^+ concentrations. At the exposed aspen site there was an increase in the pH and increase in the concentration of potassium and calcium (Table 21). Since H^+ is negatively correlated with both Ca^{++} and K^+ concentrations it would appear that the greater leaching of K^+ and Ca^{++} at the exposed site was responsible for the greater pH of the throughfall.

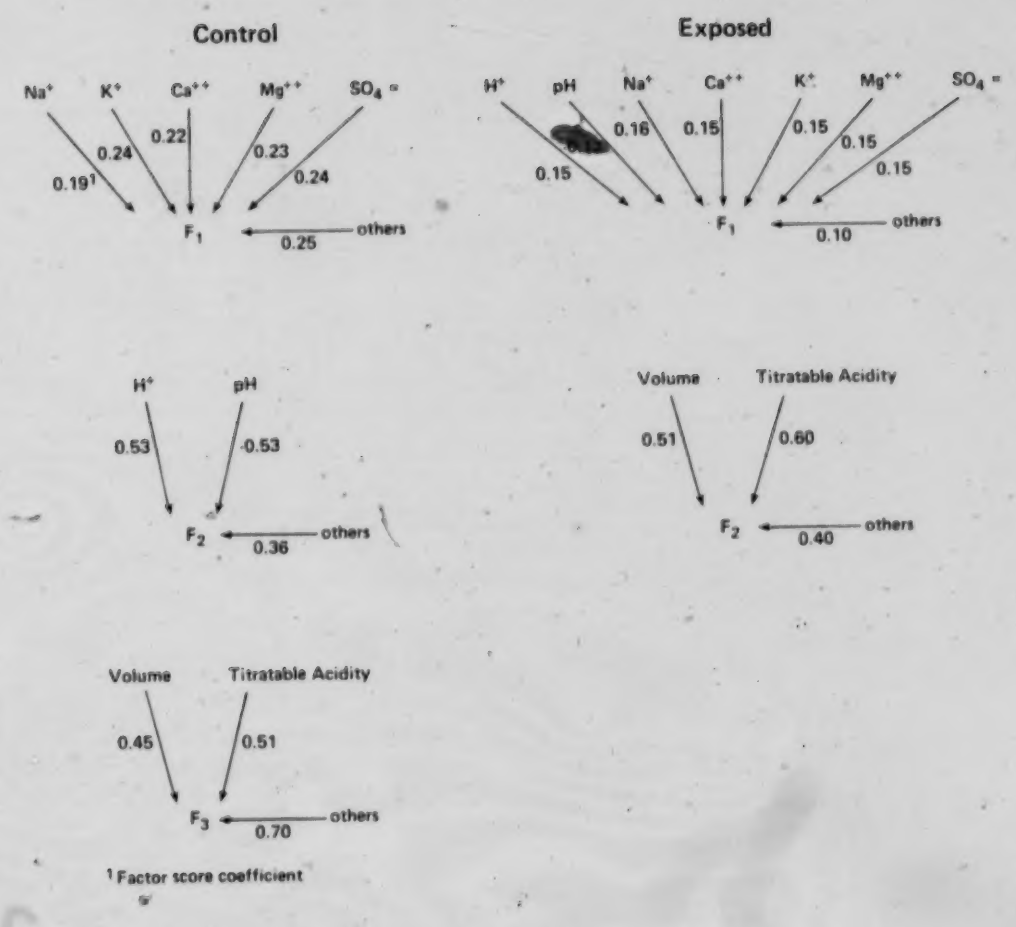
Wood and Bormann (1975) found a greater increase in the leaching of calcium and potassium (particularly calcium) from sugar maple leaves exposed to increasing acidity of an artificial acid mist in a laboratory experiment. They also

observed an increase in pH from mist to leachate although this increase was not statistically significant.

Factor three at the exposed site is related to both calcium and sulphate (Figure 6). Sulphate is negatively correlated to factor three whereas calcium is positively correlated. This third grouping of variables suggests that a second factor is influencing the sulphate sulphur content of throughfall at the exposed site. This factor is correlated to the SO4=-S content of the trembling aspen throughfall. Although the increase in SO4=-S concentration in aspen throughfall at the exposed site was small (Table 21), on several occasions there were significantly greater SO4=-S concentrations at the exposed site (Table 22).

6.1.4.2 Pine throughfall. Principal component analysis of the jack pine throughfall data produced three main factors which explain the variance in the data for the control site while for the exposed site only two factors appear to be involved (Figure 7).

For the control site, factor one is highly correlated with Na^+, K^+, Ca^{++}, Mg^{++} and SO4=-S concentrations. This represents the normal leaching of nutrients from the pine canopy and can be labelled the "leaching factor." Factor two is correlated with the hydrogen ion concentration. Jack pine throughfall is naturally acidic, in this case having a mean pH of 5.09 during the summer months. This is probably due to



[1] Factor score coefficient

Figure 7. Simplified Path diagrams showing the relationship between the principal components and variables for Pine (*Pinus banksiana* Lamb.) throughfall at a control site and a site exposed to sulphur dioxide.

the presence of organic acids and hence factor two can be regarded as the "natural acidity factor."

For exposed pine throughfall, factor one is positively correlated with the Na^+, K^+, Ca^+ and Mg^{++}, and $SO_4^{=}$-S concentrations and is positively correlated with hydrogen ion concentration. This is consistent with the observation that at the exposed site, increased concentrations of nutrients (K^+, Ca^{++}, Mg^{++}) were accompanied by a depression in pH (Table 21).

The order of removal of nutrients in the tree crown was:

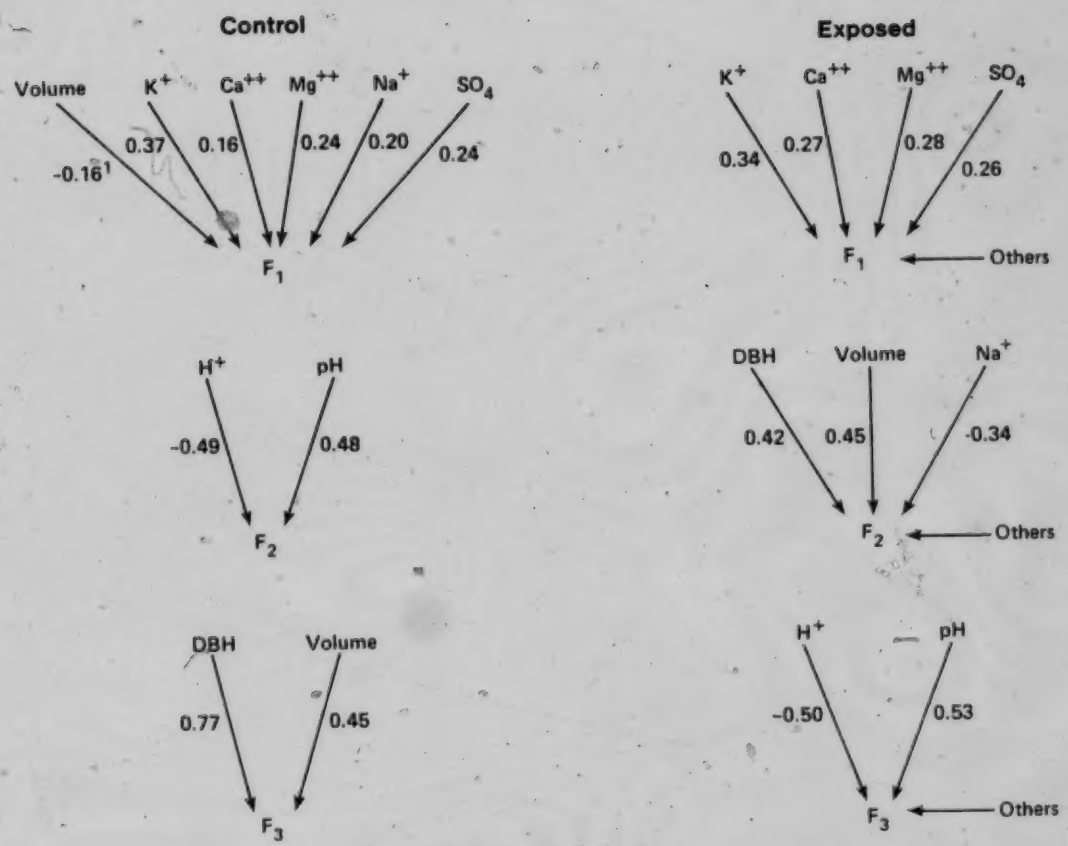
$$Ca^{++} > K^+ > SO_4^{=}\text{-}S > Mg^{++} > Na^+$$

for the control site, and for the exposed site was:

$$K^+ > Ca^{++} > SO_4^{=}\text{-}S > Mg^{++} > Na^+$$

Therefore along with the general increase in the net removal of K^+, Ca^{++} and $SO_4^{=}$-S at the exposed site there has been an increase in the leaching of K^+ relative to the other nutrients.

6.1.4.3 Aspen Stemflow. Principal component analysis grouped aspen stemflow in a similar fashion to aspen throughfall (Figure 8). At the control site factor one is correlated with the cations and sulphate sulphur concentrations and negatively correlated with volume. This perhaps represents normal leaching of nutrients. Factor two is correlated with the hydrogen ion concentration and represents the pH factor.



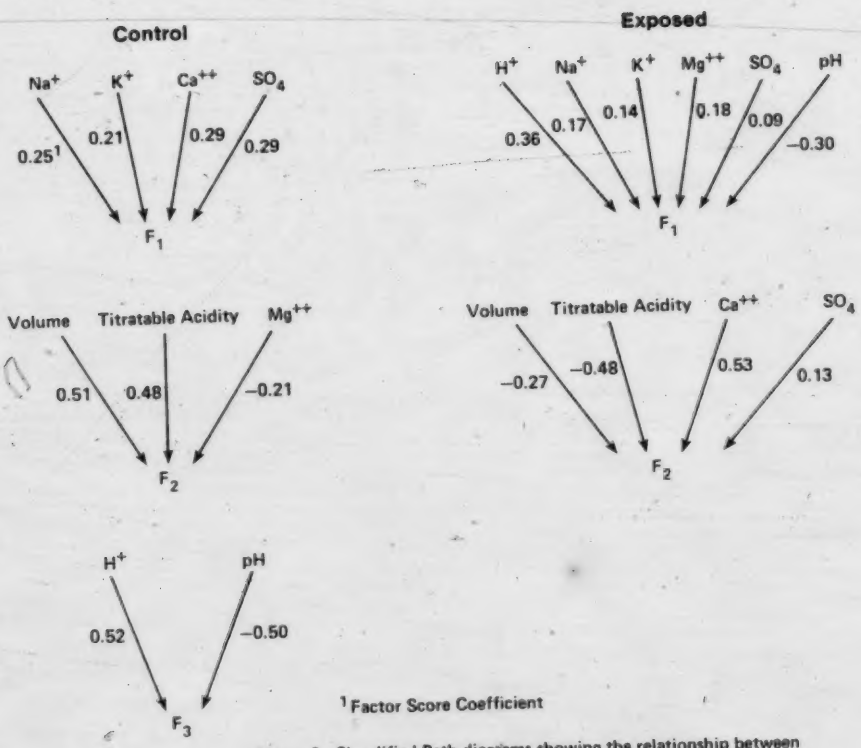
[1] Factor Score Coefficient

Figure 8 Simplified Path diagrams showing the relationship between the principal components and variables for Aspen (*Populus tremuloides* Michx.) stemflow at a control site and a site exposed to sulphur dioxide.

Aspen stemflow is naturally basic but factor two is not correlated with any of the basic cations. Perhaps this basicity is due to basic compounds for which analysis was not done. Factor three is related to the stem diameter and volume. The close relationship between these two factors was noted in Section 4.1.3 where a curvilinear relationship between basal area (which is a function of DBH squared) to stemflow volume was shown.

At the exposed site, factor one was related to K^+, Ca^{++}, Mg^{++} and $SO_4^{=}$-S concentrations as for the control site. Factor two was a volume factor as for the control site, but, in this case sodium was also negatively correlated with this factor. Sodium was the only nutrient that did not increase significantly in the exposed site stemflow (see Tables 21, 22). Since Na^+ was not leached from the canopy, the nutrient content of the stemflow probably reflects the Na^+ content of the incident rain. The mean concentration of Na^+ in the stemflow was very similar to the concentration of Na^+ in the incident rain at both sites (Table 20). The concentration of Na^+ would, therefore, be expected to be strongly correlated to the stemflow volume. The pH of exposed aspen stemflow was a separate factor as noted for the control site.

6.1.4.4 Pine Stemflow. Principal component analysis of jack pine stemflow data grouped the variables in much the same way as jack pine throughfall (Figure 9). This indicates that



[1] Factor Score Coefficient

Figure 9 Simplified Path diagrams showing the relationship between the principal components and variables for Pine (*Pinus banksiana* Lamb.) stemflow at a control site and a site exposed to sulphur dioxide.

changes in jack pine stemflow chemistry reflect changes in throughfall chemistry which was also indicated by comparing the element concentrations given in Table 21.

Factor one at the control site is related to Na^+, K^+, Ca^{++} and $SO_4^=$ concentrations and represents removal of these nutrients from jack pine bark. Factor two is related to the stemflow volume while factor three is the acidity factor. Jack pine stemflow is quite acidic with a mean pH at the control site of 4.58 (Table 21).

At the exposed site Na^+, K^+, Mg^{++}, H^+ and to a lesser extent $SO_4^=$-S concentrations are positively correlated with factor one. Therefore, the factor correlated with the acidity of jack pine stemflow is also highly correlated with the concentrations of Na^+, K^+, and Mg^{++}. This is similar to the situation for jack pine throughfall (Figure 7).

Factor two is negatively correlated with stemflow volume and positively correlated with Ca^{++} and $SO_4^=$ concentrations. The correlations between Ca^{++} and $SO_4^=$ were also noted for aspen throughfall at the exposed site. This high correlation may be because both Ca^{++} and $SO_4^=$ concentrations are both correlated to stemflow volume.

6.1.5 Deposition of Sulphur in Throughfall and Stemflow

6.1.5.1 Trembling Aspen. The deposition of $SO_4^=$-S in trembling aspen throughfall and stemflow compared to

deposition in the incident rain is given in Table 26. At both the control site and the exposed site the amount of sulphur deposited in throughfall and stemflow was higher than that deposited in incident rain. The amount deposited in both the incident rain and the throughfall and stemflow was greater at the site exposed to sulphur dioxide than at the control site. The deposition expressed as kg/ha/mo was calculated from the deposition in kg/ha at each sample period by weighting each value by the number of days in the month divided by the number of days over which the sample was collected. This method assumes that the precipitation over the sample period represents the mean precipitation/day over the month. This may not be the case particularly where only one sample per month was obtained. This method does allow comparison with other forms of sulphur deposition, however.

There was a marked increase in the per cent of the total sulphate sulphur deposited in net precipitation as stemflow at the exposed site. The per cent of incident rainfall returned to the forest floor as stemflow was similar for both aspen plots (Tables 4 and 5) and the total volume as stemflow was the same at both sites when expressed in mm. The difference in the per cent of the total sulphate sulphur deposited must therefore reflect the influence of atmospheric sulphur on aspen trees at the exposed site. When the amount of sulphate sulphur deposited in incident rain, throughfall, and stemflow at each site is weighted by the

Table 26. Deposition of sulphate sulphur in trembling aspen throughfall and stemflow for the control site and the exposed site from June through September, 1976

Month	Sample period	Deposition in Throughfall and Stemflow				Total Monthly Deposition in Net Precipitation[3]	Total Deposition in Rain
		TF[1]	SF[2]	Total	Fraction as SF[2]		
	(days)	(kg/ha)	(kg/ha)	(kg/ha)	(%)	(kg/ha/mo)	(kg/ha/mo)
				Control Site			
June	5	0.134	0.016	0.150	10.7	0.900	0.456
July	17	0.225	0.035	0.260	13.5	0.474	0.170
July	7	0.049	0.011	0.060	18.3	0.266	0.080
July	7	0.046	0.012	0.058	20.7	0.257	0.159
August	23	0.229	0.009	0.238	3.8	0.321	0.000
September	13	0.104	0.012	0.116	10.3	0.268	0.261
Mean				0.882	12.9	0.41	0.19
				Exposed Site			
June	8	0.172	-	0.172	-	0.645	0.424
July	15	0.101	0.097	0.198	49.0	0.409	0.517
July	14	0.178	0.134	0.312	42.9	0.691	0.095
August	12	0.046	0.034	0.080	42.5	0.207	-
August	15	0.066	0.032	0.098	32.7	0.203	0.066
September	14	0.297	0.077	0.374	20.6	0.801	0.632
Mean				1.234	37.5	0.49	0.35

1 Throughfall
2 Stemflow
3 Throughfall + Stemflow

volumes of each particular fraction at each site, a direct comparison between sites is possible. Such a calculation reveals that the amount of sulphate sulphur removed from the tree canopy (throughfall + stemflow - incident rain) at the exposed site was 0.97 kg/ha and 0.66 kg/ha at the control site. This increase is small in absolute terms but represents an increase of 47% at the exposed site and is approximately the same amount as the increase in total amounts of sulphur dioxide received by the exposed site (Table 20). The values for incident rain and net rainfall (throughfall + stemflow) were 0.34 kg/ha and 1.00 kg/ha for the control site and 0.88 kg/ha and 1.85 kg/ha for the exposed site respectively.

6.1.5.2 Jack pine. The deposition of sulphate sulphur in jack pine throughfall followed the same trend as for trembling aspen. At both sites there was a greater deposition of sulphur in throughfall and stemflow than in the incident rain (Table 27). The total amount of sulphate sulphur deposited in throughfall and stemflow (weighted by throughfall volumes) was 1.7 kg/ha for the control site and 2.9 kg/ha for the exposed site. The corresponding values for the amounts removed from the canopy were 1.5 kg/ha and 2.00 kg/ha for the control site and exposed site respectively. These values indicate that more sulphur was deposited under jack pine than the amounts deposited under aspen even though the aspen plots were more highly stocked (Table 1).

Table 27. Deposition of sulphate sulphur in jack pine throughfall and stemflow for the control site and the exposed site from June through September, 1976.

Month	Sample Period	Deposition in Throughfall and Stemflow				Total Monthly Deposition in Net Precipitation[3]	Total Deposition in Rain
	(days)	TF[1] (kg/ha)	SF[2] (kg/ha)	Total (kg/ha)	Fraction as SF[2] (%)	(kg/ha/mo)	(kg/ha/mo)
				Control Site			
June	11	0.335					0.325
July	17	0.414	0.012	0.436	2.9	0.752	0.152
July	7	0.083	0.001	0.083	0.8	0.356	0.100
July	7	0.071	0.013	0.184	0.7	0.789	0.135
August	23	0.504	0.028	0.532	5.3	0.694	0.000
September	13	0.148	0.005	0.153	3.1	0.353	0.000
Mean				0.278	2.7	0.59	0.12
				Exposed Site			
June	8	0.670					0.423
July	15	0.416	0.072	0.488	14.7	0.976	0.533
July	14	0.336	0.025	0.362	7.0	0.776	0.093
August	12	0.117	0.008	0.124	6.1	0.310	
August	15	0.146	0.003	0.149	1.7	0.298	0.036
September	14	0.450	0.084	0.534	15.6	1.144	0.655
Mean				0.331	9.0	0.70	0.35

[1] Throughfall
[2] Stemflow
[3] Net precipitation is the sum of throughfall and stemflow

As for aspen, the per cent of the total sulphate sulphur deposited in jack pine stemflow was higher for the exposed site. This is despite the larger volume of stemflow (expressed as a per cent of incident rainfall - see Tables 7 and 8) and larger number of stems/ha (Table 1) at the control site.

6.1.6 Effect of Sulphur Dioxide on Jack Pine Stemflow Chemistry

Jack pine stemflow sampled during June and July 1977 was progressively less acidic and contained lower levels of sulphate sulphur with increasing distance from the emission source (Table 28). The low concentrations of SO4=-S at the Muskeg Mountain site (exposed) would be due, in part, to the higher stemflow volume and similarly the higher SO4=-S concentration at Algar (control) could be due to the low stemflow volumes recorded. When these concentration values were converted to sulphate sulphur deposition as kg/ha/mo they were multiplied by the respective stemflow volumes and the number of stems/ha. These values show the general decrease with increasing distance from the emission source. This is coincident with a decrease in the average SO2 concentration in the air at each site as determined by the total sulphation discs.

The differences in pH, titratable acidity, sulphate sulphur and total sulphation were significant ($p < 0.05$)

Table 28. Acidity and sulphate sulphur content of jack pine stemflow sampled at four sites during June and July 1977. The letters indicate pairs of values which are significantly different ($p<0.05$) according to Duncan's multiple range test.

Site	Distance(km) /Direction from source	Mean Sample Volume/Tree (ml)		pH		Titratable Acidity[1] (ug H+/ml)		SO4=-S (ppm)		Total SO4=-S[2] (kg/ha/mo)		Total Sulphation (mgSO3eq/100cm²/day)	
		mean	SE[3]	mean	SE	mean	SE	mean	SE	mean	SE	mean	SE
Steepbank 3	2.4/ESE	2729	1205	3.97b	0.07	0.76ab	0.16	17.49abc	3.30	0.025a	0.006	0.058ab	0.011
Muskeg Mountain	38.0/ENE	8841	3225	3.91a	0.08	0.59	0.16	4.37b	1.03	0.020	0.006	0.056cd	0.004
Algar	101.0/SSW	1409	408	4.68ab	0.22	0.33a	0.06	5.66c	1.04	0.015	0.005	0.016bd	0.002
May 2	200.0/SW	9891	2142	4.32	0.11	0.34b	0.10	1.03a	0.28	0.008a	0.001	0.011ac	0.001

[1] Titrated with 0.001N KOH to pH 7.00
[2] Calculated on the basis of 1000 stems/ha
[3] Standard error

Table 29. Analysis of variance of pH, titratable acidity, sulphate sulphur and total sulphation between sites.

	pH	Titratable acidity	SO4=-S	Total sulphation
dF	53	53	53	54
F ratio	6.716	2.903	14.572	27.204
F probability	***	*	***	***

* significant at $p<0.05$
*** significant at $p<0.001$

between sites (Table 29 and Appendix 10.5). The trends in stemflow acidity and sulphate sulphur content are illustrated in Figure 10. This Figure includes data from a remote site at Canwood, Saskatchewan. Near the emission source (Steepbank 2 and Muskeg Mountain) the pH of jack pine stemflow is low compared to remote sites (Algar, May and Canwood). The sulphate sulphur content of jack pine stemflow at the former sites is high as compared to the latter sites.

It is interesting to note that the sulphate sulphur content and acidity of jack pine stemflow are highly correlated at sites close to the emission source but they are not correlated at the remote sites (Table 30). The acidity values used for this comparison were calculated from the pH values. These acidity values correspond to free acid in the stemflow. A high correlation does not indicate a causal relationship but this high correlation at sites close to the emission source and low correlation at the control sites suggests that the emission source is responsible for both the increased acidity and sulphate sulphur content of the stemflow at the exposed site.

6.1.7 Effect of Sulphur Dioxide on Bark Leachate Acidity and Sulphur Content

To further confirm the field findings, some bark samples from jack pine, trembling aspen and black spruce were exposed to sulphur dioxide in a controlled atmosphere

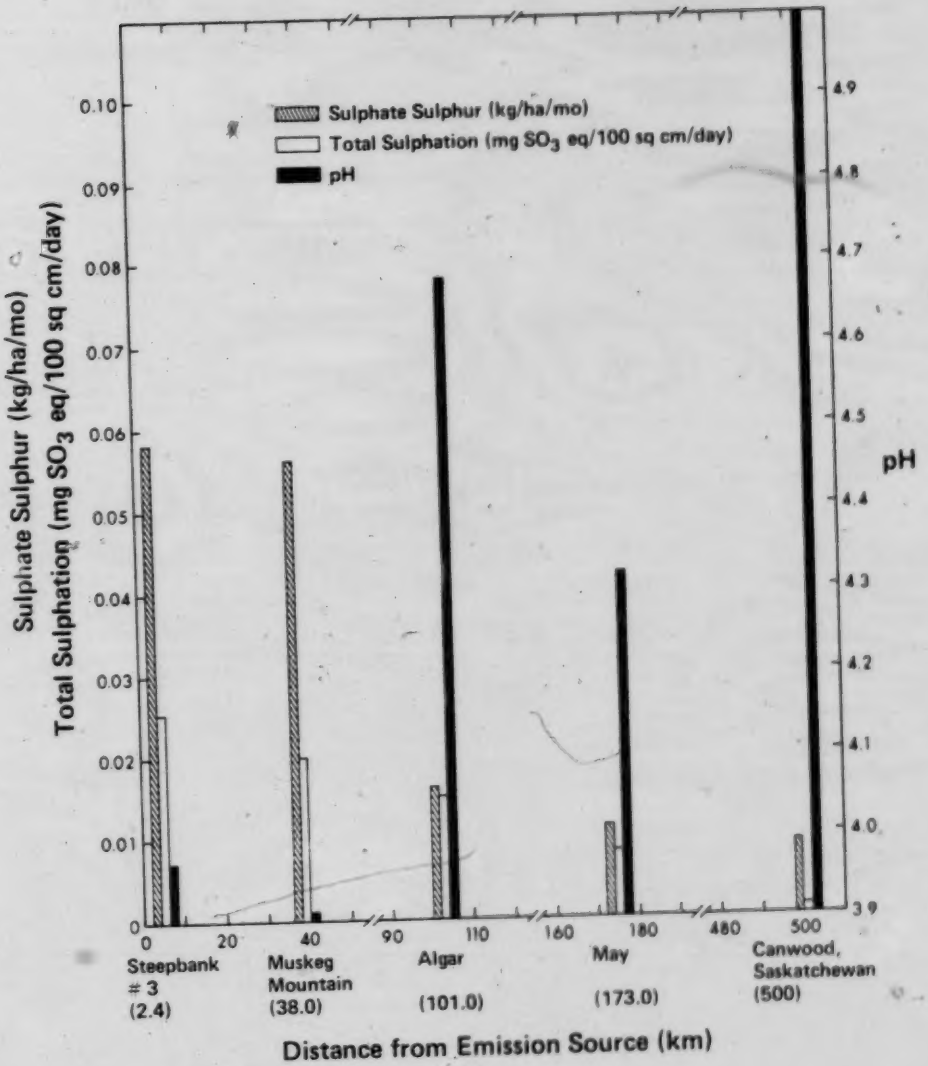


Figure 10. The variation in sulphate sulphur and acidity of jack pine (*P. banksiana* Lamb.) stemflow with increasing distance from a sulphur dioxide emission source. Sulphate sulphur was calculated on the basis of a stand density of 1000 stems/ha. Total sulphation was determined from PbO_2 sulphation discs with an exposure period of two weeks.

Table 30. Relationship between acidity and sulphate sulphur content of jack pine stemflow sampled at four sites during June and July 1977.

Site[1]	Distance (km) direction from source	correlation of hydrogen ion concentration[2] versus SO4=-S concentration		
		correlation coefficient (r)	r^2	significance level
Steepbank 3	2.4/ESE	0.80	0.64	0.001
Muskeg Mountain	38.0/ENE	0.76	0.58	0.01
Algar	101.0/SSW	0.23	0.05	0.22
May 2	200.0/SW	-0.12	0.01	0.34

[1] Refer to Figure 2 showing site locations
[2] Calculated from the pH (hydrogen ion concentration = 10-pH).

experiment.

The results (Table 31) show that jack pine bark leachate was more acid and contained higher amounts of SO4=-S after exposure to sulphur dioxide. The pH of jack pine bark leachate decreased from about 5.5 to 4.8, a change of 0.7 pH units. This decrease in pH was associated with a large increase in the SO4=-S concentration. For the jack pine bark samples from Algar the hydrogen ion concentration (as calculated from the pH values) increased by 279% while the SO4=-S concentration increased by 405% upon exposure to SO2. Spruce bark showed a similar trend but the changes were less dramatic.

The reduction in pH of the aspen bark leachate is contrary to the field results where aspen stemflow increased in pH at the site exposed to sulphur dioxide (Table 21). However, the increased sulphate sulphur concentration of the exposed bark leachate is consistent with the increased SO4=-S concentration of aspen stemflow at the exposed site (Table 21). The difference in the laboratory findings with respect to pH may be because aspen stemflow consists of rain water which has passed over the foliage and then runs down the branches and down the stem. The smooth bark of aspen and the acutely angled branches cause a channelling of water down the tree trunk. This leaf leachate could alter the composition of any bark leachate. Thomas (1969) sampled stemflow on dogwood trees which had been tagged with ^{45}Ca

Table 31. The pH and sulphate sulphur content of washings from bark samples exposed to SO2 in a controlled environment chamber[1] for seven days.

Sample	pH	change	SO4=-S[2] (ppm)	Area (cm^2)
Exposed Aspen	5.53		1.97	56.3
Control Aspen	5.87	-0.34	0.29	56.3
Exposed Spruce	4.75		1.43	56.3
Control Spruce	5.06	-0.31	0.30	56.3
Exposed Pine (May)[3]	4.87		0.56 (0.70)	30.0
Control Pine (May)	5.64	-0.77	0.23	37.5
Exposed Pine (Algar)[3]	4.81		1.87 (0.83)	25.0
Control Pine (Algar)	5.49	-0.68	0.37	56.3

[1] average SO2 concentration = 0.1 ppm
average relative humidity = 80%
average air temperature = 22°C
[2] SO4=-S concentration weighted according to bark sample area with control bark sample area considered equal to one. Actual concentration value is given in brackets.
[3] Site where bark was sampled

and found that after leaf abscission, stemflow contained ^{45}Ca at much lower concentrations than when trees supported foliage, indicating that direct leaching from the bark did not contribute as much to the chemical composition of the stemflow as did leaching of the leaves. However the laboratory experiments here, indicate that a substantial amount of the stemflow $SO_4^{=}$-S content would be derived from bark washings. The depression in the pH of bark leachate of all three species is consistent with the results of Grodzinska (1976) who found that bark increased in acidity in areas exposed to sulphur dioxide.

6.2 DISCUSSION

The results indicate that larger quantities of the cations K^+, Ca^{++} and Mg^{++} were being removed from the canopies of trembling aspen and jack pine at the site exposed to sulphur dioxide pollution. Consideration of the ionic ratios above the canopy and beneath the canopy suggests that this increase in cations was largely the result of foliar leaching. There was no increase in the leaching of Na^+ at the exposed site. This is consistent with the observations of Wood and Bormann (1975) who found an acidified artificial mist increased the leaching of K^+, Ca^{++} and Mg^+ from sugar maple seedlings but appeared to have a depressing effect on the loss of Na^+. Abrahamsen *et al.* (1976) found that when European studies were compared a pattern emerged. The sodium values in throughfall reflected

the distance from the coast whereas the pattern of increased potassium, magnesium, calcium and particularly sulphate sulphur corresponded with a parallel increase in the air pollution.

The hypothesis of cation exchange would seem to explain, in part, the increased leaching of cations from aspen at the exposed site and the increased pH of the throughfall and stemflow. Hydrogen ions in the precipitation could be exchanged with cations on exchange sites on the cell walls and cuticle, resulting in increased pH from incident precipitation to throughfall and stemflow. Such a mechanism could be responsible for an increase in the leaching of cations from jack pine but would be inconsistent with the depression in pH observed for jack pine throughfall and stemflow at the exposed site. This depression in the pH of jack pine throughfall was associated with increased deposition of $SO_4^{=}$-S at the exposed site. The hydrogen concentration of jack pine throughfall was highly correlated with $SO_4^{=}$-S concentrations ($r^2=0.86$) at the exposed site and poorly correlated with $SO_4^{=}$-S concentrations ($r^2=0.12$) at the control site (Tables 48 and 49). A similar effect was observed for jack pine stemflow. This suggests that the acid responsible for the increased leaching of cations at the exposed site is sulphuric acid.

As far as could be ascertained from the fortnightly samples, incident rain at the exposed site was not more

acidic than rain at the control site. Therefore, acid rain at the exposed site cannot account for the deposition of sulphuric acid. There are two possible explanations for this additional deposition of acid under jack pine at the exposed site as compared to the control site. Firstly, the additional acid at the exposed site may have arisen from the deposition of acid aerosols on the leaf surfaces. Sulphur aerosols in the oil sands area are predominantly of sub-micron size (Barrie 1978). Jack pine trees have a greater surface area than trembling aspen and a greater surface roughness. They would be expected to be more efficient at trapping these particulates on their needle surfaces. Hence, greater amounts of sulphate sulphur would be expected to be washed off jack pine needles than aspen leaves in a subsequent rain storm. This is consistent with the observations that greater amounts of sulphate sulphur were deposited in jack pine throughfall and stemflow than in aspen throughfall and stemflow at the exposed site. It is interesting to note that principal component analysis isolated the sulphate sulphur concentrations and calcium concerntrations in exposed aspen throughfall as an independant grouping of variables. This grouping may represent the additional leaching of calcium at the exposed site due to the deposition of acid particulates and subsequent cation exchange in the canopy. This explanation is also consistent with the fact that sulphate was positively correlated with the factor (F3) whereas calcium

was negatively correlated. Fly ash from coal combustion has been shown to contribute significantly to the amounts of soluble sulphates in throughfall (Shriner and Henderson 1978). McColl and Bush (1978) attributed the sulphate sulphur in thoughfall to removal of particulates from leaf surfaces rather than to leaf leaching.

Trees may absorb SO2 directly from the air (Materna and Kohout 1963) and elevated levels of sulphate have been found in tree leaves in areas exposed to sulphur dioxide emissions (Legge et al. 1976, Baker 1977). Some of this additional sulphur may be translocated from the leaves to other plant parts including the roots (Jensen and Kozlowski 1975). Garland and Branson (1977) found that a large portion of the absorbed sulphur could be removed if the plants were washed soon after exposure but little sulphur was accessible after a delay of some "tens of minutes". These results suggest that leaching from the leaves may not account for the additional sulphate sulphur deposited under aspen and jack pine canopies at the exposed site.

The second possible explanation for the increased acid deposition under jack pine, is that significant quantities of SO2 may be deposited in water intercepted by the forest canopy (Garland and Branson 1977). Here dissolved SO2 may be oxidized to sulphate. Absorption of sulphur dioxide could also conceivably occur when the forest canopy was wetted by dew. The interception storage capacity for jack pine at the

exposed site was about 5 mm, while for trembling aspen at the exposed site about 1 mm (Section 4.1.2). The amount of water retained would decrease during the drying period because of evaporation but the difference between the two species would remain. This mechanism of uptake of SO2 on wet surfaces could, therefore, explain the difference in the deposition of sulphate sulphur between the two species. The acid resulting from the oxidation of the absorbed SO2 could also facilitate exchange of hydrogen ions with cations on the leaf exchange sites. As stated earlier, this exchange needs only the leaf surface to be wet to occur. The leached cations could be deposited on the leaf surface when the water dries off and they could then be removed by a subsequent rain shower. As the water on the leaves evaporates, the acid could become more concentrated facilitating greater exchange. This acid could also cause increased weathering of the leaf cuticle and hence greater leaching of plant nutrients. Shriner (1976) observed that acidified artificial rain of pH 3.2 caused a marked erosion of the epicuticular waxes of Quercus phellos and Phaseolus vulgaris.

The depression in pH for jack pine throughfall at the exposed site may be due to this deposition of SO2 on the wet needles and subsequent oxidation to sulphuric acid. Dead wood, however, may retain measurable amounts of sulphur and it has been suggested that increased acidities in throughfall can be attributed to this material (Malmer

1974). Increased leaching of organic acids from jack pine needles and branches could also be in part responsible for the reduction in pH of jack pine throughfall. Leaching of organic acids from jack pine bark could not, however, explain the dramatic depression in pH of jack pine stemflow at the exposed site. Reduction in pH was shown to be strongly correlated with sulphate sulphur. The additional sulphur may have arisen from the uptake of SO2 by water intercepted by the bark surface. Jack pine bark is very rough and platy and would possess a large surface area in relation to the basal area. This would explain why greater amounts of SO4=-S were deposited in jack pine stemflow than aspen stemflow at the exposed site when the values were adjusted for differing stand densities.

Prior to exposing the bark samples to sulphur dioxide in the controlled atmosphere experiment they were washed with distilled water. Although they were air dried for several hours before exposure some moisture may have been retained by the samples. Sulphur dioxide could then have been taken up in this water and given rise to the acid bark leachates observed. Garland and Branson (1977) found that scots pine bark absorbed negligible amounts of sulphur dioxide and jack pine, black spruce, and trembling aspen bark may behave the same when thoroughly dry.

In unpolluted regions carbonic acid derived from atmospheric CO2 has been shown to be the primary source of

hydrogen ions in precipitation. These could be not expected to produce a pH of less than 5.7 (Barret and Brodin 1955). Below a pH of 5.0 carbonic acid has no effect on measured pH (Galloway et al. 1976). Bicarbonate would, therefore, be a major anion in aspen throughfall and stemflow at both the control and exposed sites, where the pH >>5.0. Unfortunately, bicarbonate was not tested for in any of the samples so the relative contribution of strong acid (H_2SO_4) and carbonic acid to the leaching of nutrients at the exposed site, could not be determined directly. The difference in leaching between the control site and the exposed site could, however, be attributed to the addition of strong acid, i.e. bicarbonate was assumed to be the same at both sites.

The pH of jack pine throughfall at the control site was about 5.0 and was always less than the pH of incident rain. This additional free acid was, therefore, not derrived from carbonic acid but from other weak organic acids which had presumably been leached from the tree crown. The low pH of jack pine stemflow at the control site indicates that stemflow also contains rather large concentrations of organic acids. Most plants take up more cations than anions. The excess of basic cations is electrically balanced by organic anions formed in the plant (Reuss 1976). According to Reuss, during the breakdown of these basic esters of organic acids (e.g. RCOOMg) organic matter may be hydrolyzed. The bases are removed and leached as

bicarbonates and the remaining dead plant material is acidic due to the presence of the organic acids. If the pH is lowered to the point where bicarbonates no longer exist (pH < 5) then the bases can only leach in conjunction with anions such as SO4= or by chelation with certain organic complexes. This process could be occurring in the jack pine canopy where old needles remain on the tree for a number of years. The cuticle on the needles may become cracked with age (Zamierowski and McCloskey 1975) permitting organic acids to be washed out by rain, giving rise to the natural acidity of jack pine throughfall.

Epiphytic lichens growing on the branches and trunk of jack pine may also have an influence on the acidity of stemflow and throughfall. Lang et al. (1976) found that lichens released Ca++, Mg++ and H+ when submerged in water. Increased acidity of the water tended to increase the release of Ca++ and Mg++. They hypothesized that the lost nutrients were replaced through absorption from bark via lichen rhizoids or absorption under conditions of mist and light rain. These results are consistent with the observation that jack pine stemflow was acid and contained high concentrations of cations.

7. GENERAL DISCUSSION

The stability of forest ecosystems is dynamic in nature and depends to a large degree on the cycling of nutrients. The results presented above strongly suggest that atmospheric sulphur dioxide is causing an increased leaching of certain nutrients from the tree crowns of two forest ecosystems in the oil sands area. This effect is occurring in an area where the concentration of sulphur dioxide in the air is lower than where acute damage and visible symptoms occur.

Since forest ecosystems are complicated structures the possible effects of such a disturbance on ecosystem processes are difficult to determine. Figure 11 represents a hypothetical model of some of the possible effects. According to these results, the processes in trembling aspen ecosystems will be affected quite differently from those of jack pine ecosystems.

In the trembling aspen ecosystem, throughfall and stemflow inceased in pH at the site exposed to sulphur dioxide. The acidity of rain also decreased as it passed through the canopy of trembling aspen. This removal of hydrogen ions by exchange in the canopy could lessen the potential inpact of acid precipitation on soils under aspen stands in the oil sands area. The additional leached nutrients from the tree crowns could increase the amount of nutrients in the available nutrient pool in the soil. This

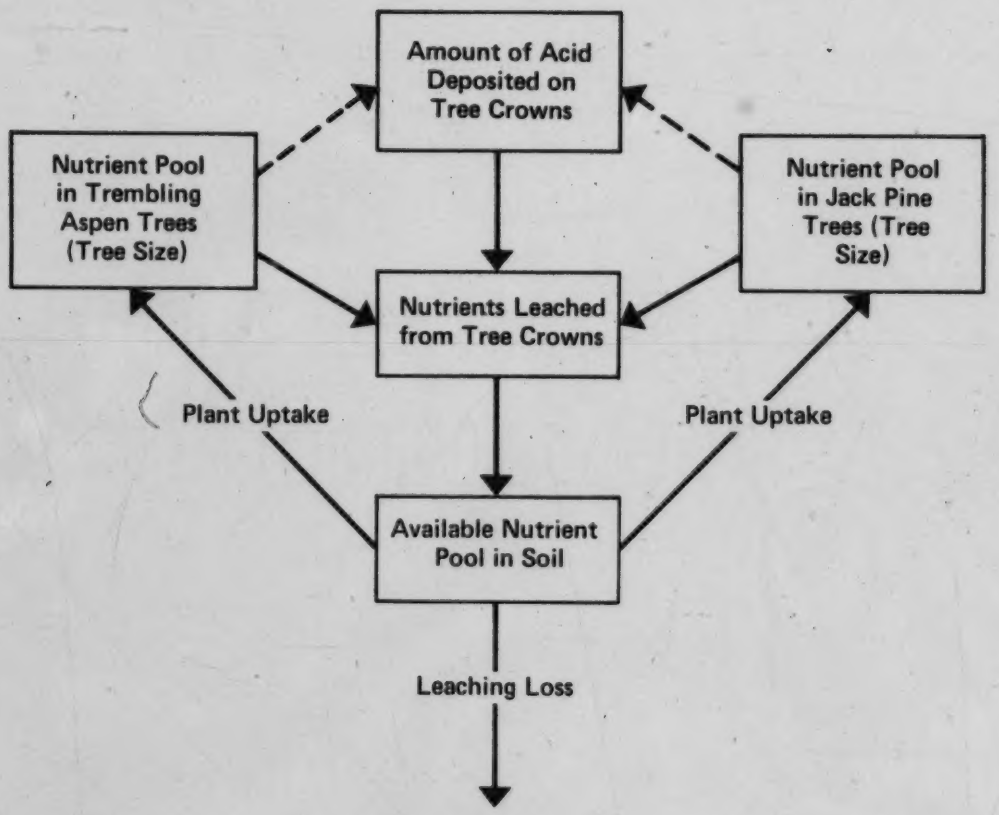

Amount of Acid Deposited on Tree Crowns
Nutrient Pool in Trembling Aspen Trees (Tree Size)
Nutrient Pool in Jack Pine Trees (Tree Size)
Nutrients Leached from Tree Crowns
Plant Uptake
Plant Uptake
Available Nutrient Pool in Soil
Leaching Loss

Figure 11 Simple model illustrating the relationship between atmospheric sulphur emissions and macroelement flux in two forest ecosystems.

could result in increased plant uptake of nutrients. Mecklenburg and Tukey (1964) found that the rate of root uptake and translocation of ^{45}Ca to bean stems and foliage was greater per gram dry weight in plants which were leached than in plants which were not leached. This was true whether the leached plants grew at a rate which is faster than, slower than, or the same as plants which were not leached. The additional leaching of nutrients from tree crowns may represent a positive effect if increased plant uptake is a consequence. The cycling of nutrients in these boreal forest ecosystems is slow because of the slow rate of litter decomposition. Increased uptake of nutrients could lead to increased growth. Young vigorously growing tissues accumulate calcium from exchange sites, thus reducing the amount of exchangeable calcium available for leaching (Mecklenburg et al. 1966). This would suggest that increased growth would result in decreased leaching of nutrients from the tree crown. Increased growth could also change the temporal distribution of leaching, since all the leaves become senescent at the end of the growing season a greater amount of leaching could occur in the fall. In addition, increased growth could increase the leaf surface area and hence increase the deposition of acid. Since foliar leaching competes with cellular metabolism and vice-versa (Mecklenburg et al. 1966) excessive leaching after long periods of rainfall may reduce plant growth.

Jack pine throughfall and stemflow increased in acidity

at the site exposed to sulphur dioxide. Effects of the increased acidity on soil processes would be extremely complex. Overrein (1972) found in lysimeter experiments that leaching of calcium in several different soil types increased drastically when the acidity of precipitation increased. Leaching of nutrients from soil by acid precipitation is reduced to some extent, however, by the presence of neutral salts in precipitation (Wiklander 1975). Field studies on forest ecosystems in southern Sweden have shown that acid canopy drip gives rise to an increase in the degree of leaching of calcium from the soil (Nihlgard 1971). Jack pine commonly grows on coarse acidic soils (Pawluk and Arneman 1961). These soils are poorly buffered against acid and would be susceptible to leaching of bases by increased deposition of acid. Such a process of soil acidification could be occurring in the oil sands area at sites close to the emission source.

The processes discussed above illustrate the complexity of the systems involved. The processes may change over time leading to a restoration of stability to the system or they may accelerate leaching leading to the eventual decline of the tree species. It can be seen that sulphur deposition has marked differences on processes in jack pine and trembling aspen ecosystems. Further research is needed into the effects of sulphur emissions on nutrient cycling, before any definitive conclusions on ecosystem response can be made.

8. CONCLUSIONS

This study was initiated to determine the relative amounts of nutrients returned to the soil by throughfall, stemflow and litterfall of trembling aspen, jack pine and black spruce in northern Alberta. The amounts of nutrients recycled from trees to soil by these pathways were also determined. The influence of atmospheric sulphur emissions from an oil sands extraction plant on nutrient return in throughfall and stemflow was also investigated. The objective was to determine the differences, if any, of the affect of sulphur emissions on nutrient return in the three ecosystems studied. This information has particular relevance in the Athabasca Oil Sands area where two oil sands extraction plants are currently operating and a third is in the planning stages.

Nutrient return in throughfall and stemflow is coupled with the hydrologic cycle. The nature of this study, therefore, necessitated determination of the distribution of rainfall under the three tree species investigated. The amount of net precipitation (expressed as a percentage of incident rain) reaching the forest floor under trembling aspen, jack pine and black spruce was 91%, 85% and 76% respectively. Throughfall averaged about 84-85% of incident precipitation for both trembling aspen and jack pine and about 76% for black spruce. The amount of throughfall per sample period was highly correlated with the amount of

precipitation per sample period. The throughfall regression equation developed for trembling aspen ($T=-0.687 + 0.877P$, $r^2=0.999$) was in good agreement with that developed for hardwood stands elsewhere in North America. The equation developed in this study could be used to estimate throughfall in similar trembling aspen stands elsewhere in Alberta. The amount of stemflow was greatest in trembling aspen at about 7-8% of incident precipitation. Stemflow in jack pine amounted to about 0.2-0.4% and for black spruce less than 0.1%. In general, stemflow per stem per sample period increased with increasing amounts of precipitation and stem size, the former having the greatest effect.

The relative heterogeneity of throughfall and stemflow volumes from the three species was investigated by determining the number of gauges required to obtain a standard error of the mean equal to ten per cent of the mean. The number of throughfall gauges used in this study (20) was only sufficient to satisfy this requirement for trembling aspen. Stemflow was extremely variable and lower precision had to be accepted in estimates of this parameter. In general, variability in throughfall and stemflow decreased with increasing amounts of precipitation for all species.

The relative amounts of nutrients added to the forest floor in throughfall, stemflow, and litterfall over the summer period (May to October) were determined for trembling

aspen, jack pine, and black spruce. The order of return of nutrients (Ca>Mg>K>Na) was the same for all three species. In general, litterfall was the most important source of magnesium and calcium for all three species. Significant amounts of calcium and magnesium were present in jack pine throughfall. About 25 per cent of the magnesium added to the forest floor in black spruce was in throughfall. The majority of sodium added to the soil was in litterfall in the aspen ecosystem. The aspen canopy absorbed sodium from incident rain, resulting in low amounts in throughfall and stemflow. Almost all the sodium reaching the forest floor in jack pine and black spruce was via throughfall, and this was largely derived from incident precipitation. The amount of nutrients in throughfall was highly correlated with the amount of precipitation. No seasonal trends in the chemical components of throughfall were observed. Throughfall was the most important transfer mechanism for potassium in all three species. Throughfall supplied about 70% of the potassium to the ground in jack pine, more than double that supplied by litterfall. The concentration of nutrients was higher in stemflow than in throughfall. When expressed on an equivalent area basis, stemflow was relatively unimportant in the addition of nutrients to the forest floor in comparison to throughfall and litterfall. Stemflow takes on greater significance, however, when the amounts of nutrients deposited are calculated on the basis of its direct zone of influence.

As rain passed through the canopy of trembling aspen it became enriched with cations and decreased in acidity. The process of cation exchange appears to be in part responsible for the leaching of cations from trembling aspen where apparently hydrogen ions from the rain replaced cations on exchange sites of aspen leaves and released cations to stemflow and throughfall. Rain increased in acidity as it passed through the canopy of jack pine. This was most likely due to the leaching of organic acids from tree crowns.

Significantly greater amounts of potassium, calcium and magnesium were removed from the canopies of jack pine and trembling aspen at a site close to a sulphur dioxide emission source as compared to trees at a more remote site. For black spruce only the calcium concentration in throughfall was higher at the exposed site. The greater size of the trees at the exposed site compared to the control site probably obscured any other differences from becoming evident for black spruce. The amount of sodium removed from the canopy at the exposed site was not greater than at the control site for any of the three species. The larger quantities of the cations deposited under jack pine and trembling aspen at the exposed site were most likely due to a higher rate of leaching from the canopy. Such a process competes directly with cellular metabolism (Mecklenberg et al. 1966). Consequently the increased leaching at the exposed site could lead to reduced tree growth. However,

increased leaching of cations could lead to accelerated intrasystem nutrient cycling and this may have a positive effect in these boreal forest ecosystems where nutrient turnover is slow. Further research is needed into this effect before any definitive conclusions on ecosystem response can be made.

The amounts of sulphate sulphur deposited under jack pine and trembling aspen were greater at the site located nearest the emission source. There was also a greater deposition of free acid under jack pine at the site exposed to sulphur dioxide compared to the control site. The pH of throughfall averaged 0.3 pH units lower at the exposed site and stemflow averaged 0.7 pH units less than corresponding control site values. The free acid concentrations of jack pine stemflow and throughfall were highly correlated with the sulphate sulphur concentrations at the site close to the emission source. No such correlation was evident at the site remote from the emission source. In addition, the sulphate sulphur content and acidity of jack pine stemflow was shown to decrease with increasing distance from the emission source. These results suggest that sulphur emissions are causing increased deposition of sulphuric acid beneath jack pine trees downwind from the emission source. Jack pine commonly grows in coarse acidic soils in the Oil Sands area. These soils are low in base content and are poorly buffered against acid. The increased deposition of acid under jack pine in areas close to the emission source could lead to the

leaching of bases from these soils and increased soil acidity. These soils need to be monitored to determine if such a process of soil acidification is occurring in the Oil Sands area.

In general, sulphur emissions are altering the rates of nutrient return in throughfall and stemflow of jack pine and trembling aspen stands in the oil sands area. Further research is needed into the influence of sulphur dioxide on throughfall and stemflow chemistry. In particular the mechanism by which sulphur dioxide causes increased leaching of nutrients from tree leaves needs to be investigated. Research is also needed to determine the magnitude and nature of changes in soil properties which may be induced by a change in the chemistry of net precipitation under jack pine and trembling aspen stands in the oil sands area.

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10. APPENDIX

10.1 SOIL PROFILE DESCRIPTIONS

Profile descriptions of the soils at each experimental plot of the nutrient cycling study 1976. A single soil pit was dug at each plot. Soil descriptions are according to the Canadian System of Soil Classification.

Table 32. Soil profile description - control aspen plot.

Orthic grey luvisol on sandy clay loam till.

Horizon	Depth (cm)	Description
L-H	10-0	Brownish black (10 YR 2/2 d), organic mat of decomposed aspen leaves, shrubs and mosses
Ae	0-3	Light gray (7.5 YR 8/2 d), sandy loam; granular to very weak fine platy; friable; moderate, wavy boundary; 2-5 cm thick; pH 5.1
Bt	3-30	Light yellow orange (10 YR 8/4 d), clay loam; moderate fine subangular blocky; friable; gradual, wavy boundary; pH 4.9
BC	30+	Dull yellow orange (10 YR 6/4 d), sandy clay loam; massive; friable; sand pockets; pH 5.0

Table 33. Soil profile description - exposed aspen plot.

Orthic grey luvisol on sandy clay loam till.

Horizon	Depth (cm)	Description
L-H	7-0	Brownish black (7.5 YR 2/2 d), organic mat of decomposed aspen leaves, mosses and shrubs
Ae	0-8	Light grey (10 YR 8/2 d), loam; very weak, very fine platy; friable; moderate, wavy boundary; 7-12 cm thick; some stones; pH 5.1
AB	10-22	Dull yellow orange (10 YR 7/4 d), sandy clay loam; weak fine prismatic breaking into moderate fine subangular blocky; friable; some stones; pH 5.1
Bt	22-38	Dull yellow orange (10 YR 7/3 d), sandy clay loam; weak fine prismatic; firm; some stones; pH 5.1
BC	38+	Dull yellow orange (10 YR 7/3 d), sandy clay loam; weak very fine blocky; firm; large pockets sand; pH 4.9

Table 34. Soil profile description - control jack pine plot.

Eluviated eutric brunisol developed in glaciofluvial sand.

Horizon	Depth (cm)	Description
L-H	3-0	Brownish black (7.5 YR 3/1 d), organic mat of coniferous needles and decomposed lichens; pH 5.5
Ae	0-12	Light grey (5 YR 8/1 d), sand; single grain; very loose; abrupt wavy boundary; pH 4.3
Bm	12-26	Orange (7.5 YR 6/8 d), sand; single grain; weakly cemented; pH 5.6
BC	26-36	Orange (10 YR 7/6 d), sand; single grain; loose; pH 6.0
C	36+	Dull yellow orange (10 YR 7/4 d), sand; single grain; loose; pH 6.2

Table 35. Soil profile description - exposed jack pine plot.

Gleyed grey luvisol developed in glacial till.

Horizon	Depth (cm)	Description
L-H	4-0	Dark reddish brown (5 YR 3/2 d) organic mat of pine needles and decomposed lichens and mosses
Ae	0-6	Light gray (10 YR 8/1 d) silty loam; very weak, very fine platy; friable; pH 5.1
AB	6-22	Light yellow orange (10 YR 8/4 d), loam; medium coarse, weak subangular blocky breaking into very weak, very fine granular; friable some stones; pH 5.4
Btgj	22-50	Dull yellow orange (10 YR 7/4 d), sandy clay loam; few, medium, distinct yellowish brown (10 YR 5/6 m) mottles; medium, moderate subangular blocky breaking into fine subangular blocky; friable; some stones; pH 5.1
Cg	50+	Dull yellow orange (10 YR 6/4 d) sandy clay; common medium; distinct orange (7.5 YR 6/8 m) mottles; fine moderate prismatic breaking into medium moderate subangular blocky; friable; some stones; pH 5.1

Table 36. Soil profile description - control spruce plot.

Rego glysol developed in glacial till.

Horizon	Depth (cm)	Description
O	15-0	Brownish black (7.5 YR 3/2 d) organic layer of undercomposed pert derrived from sphagnum and feather mosses; pH 3.9
Cg	0-25	Dull yellow orange (10 YR 7/3) sandy loam; massive; very hard; very firm; some stones; pH 4.8

Table 37. Soil profile description - exposed spruce plot.

Gleyed grey luvisol developed in glacial till.

Horizon	Depth (cm)	Description
LFH	9-0	Dark brown (7.5 YR 3/3 d) organic layer of partially decomposed coniferous needles and sphagnum and feather mosses
Ae	0-8	Light grey (10 YR 8/1 d), loam; very weak, very fine platy; very friable; gradual, wavy discontinuous boundary; 2.5 to 8.0 cm thick; pH 4.9
AB	8-20	Dull yellow orange (10 YR 7/3 d) sandy clay loam; medium, moderate, subangular blocky; friable; some stones; pH 6.1
Btgj	20-45	Dull yellow orange (10 YR 6/4 d) sandy clay loam; common, medium, distinct brown (10 YR 4/6 m) mottles; fine subangular blocky; some stones; pH 6.5
Cg	45+	Dull yellow orange (10 YR 6/3 d) sandy clay loam; common, medium, distinct yellow brown (10 YR 5/6 d) mottle; weak very fine subangular blocky; some stones; pH 8.3

10.2 CHARACTERISTICS OF REPRESENTATIVE SOIL SAMPLES

Physical and chemical analyses of representative soil samples from the experimental plots of the nutrient cycling study 1976.

Table 38. Physical analyses of representative soil samples from the nutrient cycling study plots.

Plot	Horizon	Sand (%)	Silt (%)	Clay (%)	Texture	Bulk Density (gm/cm^3)
Control Aspen	LFH					0.12
	Ae	63.8	18.8	17.4	SL	0.52
	Bt	21.8	41.8	36.4	CL	1.33
	BC	48.8	24.8	26.4	SCL	1.75
Exposed Aspen	LFH					0.12
	Ae	37.8	42.6	19.6	L	1.12
	AB	51.6	24.8	23.6	SCL	1.26
	Bt	56.8	17.6	25.6	SCL	1.41
	BC	47.8	22.6	29.6	SCL	13.9
Control Pine	LFH					0.36
	Ae	90.1	3.3	5.6	S	0.97
	Bm	90.9	1.5	7.6	S	1.39
	BC	93.4	1.4	5.2	S	1.57
	C	93.9	2.4	3.7	S	1.54
Exposed Pine	LFH					0.37
	Ae	29.8	53.6	16.6	SiL	0.73
	AB	45.8	28.8	25.4	L	1.17
	Btgj	47.8	18.6	33.6	SCL	1.32
	Cg	47.8	16.6	35.6	SC	1.31
Control Spruce	O					0.18
	Cg	76.8	6.0	17.2	SL	0.92
Exposed Spruce	LFH					0.07
	Ae	34.8	48.6	16.6	L	0.94
	AB	56.8	19.6	23.6	SCL	1.04
	Btgj	50.8	15.2	34.0	SCL	1.01

Table 39. Chemical analysis of representative soil samples from the nutrient cycling study plots.

Plot	Horizon	Cations[1]				pH	$SO_4^{=}$-S[2]	Electrical conductivity[3]
		Na^+ (ppm)	K^+ (ppm)	Ca^{++} (ppm)	Mg^{++} (ppm)		(ppm)	(mmhos/cm)
Control Aspen	LFH						24.4	
	Ae	3.45	1.27	5.40	0.91	5.08	2.3	0.05
	Bt	5.08	0.74	6.01	0.93	4.87	2.5	0.03
	BC	3.03	1.86	3.19	0.53	4.99	0.1	0.02
Exposed Aspen	LFH						20.0	
	Ae	0.83	0.58	4.91	0.79	5.05	2.8	0.06
	AB	0.51	0.44	2.85	0.51	5.14	1.4	0.03
	Bt	0.57	0.39	3.11	0.61	4.88	1.4	0.03
	BC	1.01	0.51	3.64	0.76	4.89	1.4	0.03
Control Pine	LFH						10.0	
	Ae	0.46	0.82	1.54	0.31	4.31	0.0	0.02
	Bm	0.56	0.39	1.62	0.33	5.62	1.8	0.01
	Bc	0.29	0.15	1.17	0.15	6.03	0.5	0.01
	C	0.34	0.14	1.25	0.14	6.19	0.0	0.01
Exposed Pine	LFH						15.6	
	Ae	0.69	0.58	2.69	0.48	5.07	1.5	0.02
	AB	0.86	0.45	2.58	0.49	5.39	0.8	0.03
	Btgj	0.97	0.26	2.78	0.39	5.07	0.9	0.02
	Cg	1.06	0.33	2.71	0.33	5.11	0.7	0.02
Control Spruce	O						32.0	
	Cg	1.77	0.47	2.51	0.43	4.82	0.1	0.03
Exposed Spruce	LFH						43.2	
	Ae	1.14	0.62	7.54	1.61	4.88	4.0	0.1
	AB	0.54	0.30	5.01	1.31	6.12	1.9	0.1
	Btgj	1.45	0.38	7.18	1.70	6.49	2.1	0.1

[1] Cations were determined from the saturated paste extract. Values are expressed as ug/g soil.
[2] Soluble $SO_4^{=}$-S was determined from 0.01 N $CaCl_2$ extracts. Values are expressed as ug/g soil.
[3] Electrical conductivity measured at 25°C.

10.3 ACIDITY AND NUTRIENT CONTENT OF RAIN, AND OF THROUGHFALL AND STEMFLOW FOR TREMBLING ASPEN, JACK PINE AND BLACK SPRUCE.

The quantities of nutrients (kg/ha) in each precipitation type were calculated by multiplying the concentration values in mg/l by the volume of each raintype in l/ha. Throughfall data are means of twenty replicates and stemflow data are means of ten replicates.

Table 40. Acidity and nutrient content of incident rain and trembling aspen throughfall and stemflow at the control site.

Date	Precipitation Type	Precipitation (mm)	Na kg/ha	K kg/ha	Ca kg/ha	Mg kg/ha	SO4=-S kg/ha	pH	Total Acidity kg/ha H+
June 29	Incident Rain	30.4	0.024	0.033	0.116	0.006	0.076	5.19	
	Throughfall		0.024	0.184	0.240	0.032	0.134	5.99	0.128
	Stemflow		0.002	0.047	0.235	0.030	0.016	7.70	0.000
July 16	Incident Rain	48.8	0.049	0.112	0.195	0.029	0.093	5.82	
	Throughfall		0.054	0.530	0.450	0.074	0.225	6.51	0.328
	Stemflow		0.005	0.119	0.465	0.067	0.035	7.78	0.000
July 23	Incident Rain	10.1	0.034	0.057	0.065	0.010	0.018	5.63	
	Throughfall		0.009	0.124	0.116	0.019	0.049	6.37	0.017
	Stemflow		0.001	0.029	0.097	0.015	0.011	7.55	0.000
July 30	Incident Rain	34.9	0.045	0.032	0.212	0.081	0.036	5.47	
	Throughfall		0.056	0.256	0.265	0.038	0.046	6.03	0.187
	Stemflow		0.005	0.091	0.352	0.051	0.012	7.56	0.000
August 28	Incident Rain	138.8	0.208	0.097	0.555	0.111	0.000	5.90	
	Throughfall		0.095	1.197	0.750	0.145	0.229	5.99	3.089
	Stemflow		0.006	0.093	0.251	0.034	0.009	7.50	0.000
September 9	Incident Rain	45.0	0.054	0.032	0.189	0.027	0.113	5.64	
	Throughfall		0.038	0.732	0.321	0.056	0.104	6.74	0.177
	Stemflow		0.004	0.092	0.231	0.029	0.012	7.47	0.000
October 2	Incident Rain	6.7	0.007	0.005	0.024	0.003	-	4.87	
	Throughfall		0.006	0.123	0.045	0.008	-	5.26	-
	Stemflow		0.001	0.012	0.033	0.005	-	6.85	-

Table 41. Acidity and nutrient content of incident rain and trembling aspen throughfall and stemflow at the exposed site.

Date	Precipitation Type	Precipitation (mm)	Na kg/ha	K kg/ha	Ca kg/ha	Mg kg/ha	SO4=-S kg/ha	pH	Total Acidity kg/ha H+
June 30	Incident Rain	26.2	0.092	0.102	0.173	0.024	0.113	5.56	
	Throughfall		0.028	0.287	0.310	0.045	0.172	6.60	0.058
	Stemflow		-	-	-	-	-	-	-
July 15	Incident Rain	41.6	0.096	0.087	0.183	0.017	0.250	5.32	
	Throughfall		0.031	0.456	0.434	0.059	0.101	6.39	0.250
	Stemflow		0.005	0.187	0.053	0.134	0.097	7.87	0.000
July 29	Incident Rain	43.0	0.039	0.043	0.211	0.026	0.043	5.60	
	Throughfall		0.035	0.367	0.531	0.065	0.178	6.41	0.237
	Stemflow		0.005	0.164	0.909	0.133	0.134	8.03	0.000
August 10	Incident Rain	20.8	0.030	0.030	0.081	0.020	-	5.36	
	Throughfall		0.023	0.252	0.286	0.046	0.040	6.46	0.054
	Stemflow		0.003	0.061	0.247	0.030	0.034	8.12	0.000
August 25	Incident Rain	21.4	0.015	0.041	0.011	0.017	0.032	5.39	
	Throughfall		0.025	0.375	0.300	0.047	0.066	6.81	0.051
	Stemflow		0.003	0.062	0.258	0.031	0.032	7.76	0.000
September 8	Incident Rain	105.2	0.063	0.032	0.210	0.021	0.295	5.44	
	Throughfall		0.072	1.101	3.564	0.127	0.297	6.78	0.724
	Stemflow		0.006	0.150	0.605	0.015	0.077	7.81	0.000
October 10	Incident Rain	27.8	0.025	0.022	0.117	0.022	-	5.87	
	Throughfall[1]		0.043	5.380	3.040	0.834	-	7.12	-
	Stemflow		0.006	0.340	0.523	0.075	-	6.93	-

[1] Throughfall values are unusually high because of leachates from leaf litter caught in the throughfall gauges

Table 42. Acidity and nutrient content of incident rain and jack pine throughfall and stemflow at the control site.

Date	Precipitation Type	Precipitation (mm)	Na kg/ha	K kg/ha	Ca kg/ha	Mg kg/ha	SO4=-S kg/ha	pH	Total Acidity kg/ha H+
June 29	Incident Rain	45.0	0.041	0.036	0.234	0.027	0.113	5.19	
	Throughfall		0.074	0.323	0.564	0.116	0.335	5.10	0.747
	Stemflow		-	-	-	-	-	-	-
July 16	Incident Rain	45.4	0.041	0.045	0.095	0.009	0.086	5.57	
	Throughfall		0.070	0.357	0.561	0.143	0.414	5.04	0.791
	Stemflow		0.001	0.003	0.015	0.002	0.010	5.00	0.018
July 23	Incident Rain	8.8	0.011	0.009	0.056	0.007	0.025	5.63	
	Throughfall		0.014	0.061	0.097	0.022	0.083	4.98	0.043
	Stemflow		0.000	0.000	0.001	0.000	0.001	5.02	0.000
July 30	Incident Rain	28.7	0.023	0.014	0.126	0.011	0.029	5.47	
	Throughfall		0.054	0.214	0.447	0.111	0.171	5.00	0.860
	Stemflow		0.001	0.003	0.021	0.005	0.010	4.65	0.035
August 27	Incident Rain	121.6	0.316	0.170	0.389	0.024	0.000	5.90	
	Throughfall		0.322	0.672	1.416	0.414	0.504	5.35	6.427
	Stemflow		0.004	0.014	0.052	0.003	0.023	4.69	1.006
September 9	Incident Rain	39.6	0.040	0.028	0.135	0.016	0.000	5.65	
	Throughfall		0.048	0.168	0.383	0.104	0.148	5.40	0.576
	Stemflow		0.001	0.003	0.010	0.002	0.004	4.65	0.038

Table 43. Acidity and nutrient content of incident rain and jack pine throughfall and stemflow at the exposed site.

Date	Precipitation type	Precipitation (mm)	Na	K	Ca	Mg	SO4=-S	pH	Total Acidity
			kg/ha	kg/ha	kg/ha	kg/ha	kg/ha		kg/ha H+
June 30	Incident Rain	26.2	0.092	0.102	0.173	0.024	0.113	5.56	0.478
	Throughfall		0.067	0.467	0.690	0.260	0.672	4.31	-
	Stemflow		-	-	-	-	-	-	
July 15	Incident Rain	41.6	0.096	0.087	0.183	0.017	0.250	5.32	1.205
	Throughfall		0.067	0.583	0.459	0.130	0.417	4.72	0.155
	Stemflow		0.001	0.012	0.025	0.005	0.029	3.50	
July 29	Incident Rain	43.0	0.039	0.043	0.211	0.026	0.043	5.60	0.991
	Throughfall		0.045	0.485	0.346	0.084	0.337	4.81	0.052
	Stemflow		0.000	0.005	0.002	0.002	0.010	3.41	
August 10	Incident Rain	20.8	0.030	0.030	0.081	0.020	-	5.36	0.161
	Throughfall		0.020	0.198	0.409	0.047	0.117	5.10	0.006
	Stemflow		0.000	0.002	0.003	0.001	0.003	3.64	
August 25	Incident Rain	21.4	0.015	0.041	0.107	0.017	0.032	5.39	0.219
	Throughfall		0.021	0.204	0.194	0.044	0.147	5.09	0.001
	Stemflow		0.000	0.001	0.001	0.000	0.001	3.66	
September 8	Incident Rain	105.2	0.063	0.032	0.210	0.021	0.295	5.44	4.694
	Throughfall		0.081	0.450	0.375	0.072	0.451	4.97	2.517
	Stemflow		0.002	0.026	0.027	0.007	0.033	3.90	
October 10	Incident Rain	27.8	0.025	0.022	0.117	0.022	-	5.87	-
	Throughfall		0.044	0.903	0.289	0.062	-	5.51	-
	Stemflow		0.001	0.009	0.010	0.002	0.008	4.12	

Table 44. Acidity and nutrient content of incident rain and black spruce throughfall and stemflow at the control site.

Date	Precipitation Type	Precipitation (mm)	Na kg/ha	K kg/ha	Ca kg/ha	Mg kg/ha	SO4=-S kg/ha	pH	Total Acidity kg/ha H+
June 29	Incident Rain	30.4	0.024	0.033	0.116	0.006	0.076	5.19	
	Throughfall		0.026	0.158	0.167	0.026	0.110	5.06	0.378
	Stemflow		-	-	-	-	-	-	-
July 16	Incident Rain	48.8	0.049	0.112	0.195	0.029	0.093	5.82	
	Throughfall		0.053	0.493	0.321	0.083	0.325	5.61	0.711
	Stemflow		0.000	0.001	0.002	0.000	0.001	5.00	0.001
July 23	Incident Rain	10.1	0.016	0.038	0.036	0.005	0.018	5.63	
	Throughfall		0.011	0.077	0.072	0.015	0.065	5.23	0.041
	Stemflow		0.000	0.001	0.001	0.001	0.000	4.66	-
July 30	Incident Rain	34.9	0.054	0.068	0.216	0.036	0.045	5.47	
	Throughfall		0.039	0.220	0.231	0.050	0.103	5.01	0.490
	Stemflow		0.000	0.002	0.003	0.001	0.001	4.63	0.001
August 27	Incident Rain	138.8	0.208	0.097	0.555	0.111	0.208	5.90	
	Throughfall		0.126	1.461	1.089	0.262	1.107	5.00	13.926
	Stemflow		0.004	0.074	0.127	0.031	0.117	4.66	0.627
September 9	Incident Rain	45.0	0.054	0.032	0.189	0.027	0.113	5.64	
	Throughfall		0.048	0.443	0.272	0.066	0.247	5.12	0.922
	Stemflow		0.000	0.004	0.008	0.001	0.004	4.53	0.006

Table 45. Acidity and nutrient content of incident rain and black spruce throughfall and stemflow at the exposed site.

Date	Precipitation Type	Precipitation (mm)	Na kg/ha	K kg/ha	Ca kg/ha	Mg kg/ha	SO4=-S kg/ha	pH	Total Acidity kg/ha H+
July 29	Incident Rain	28.4	0.031	0.026	0.131	0.011	0.028	5.60	
	Throughfall		0.057	0.256	0.267	0.048	0.279	4.87	0.417
	Stemflow		0.002	0.008	0.029	0.002	0.008	4.70	0.009
August 10	Incident Rain	7.6	0.044	0.039	0.079	0.023	-	5.42	
	Throughfall		0.014	0.037	0.237	0.022	0.050	-	0.043
	Stemflow		0.000	0.000	0.000	0.000	0.000	-	0.000
August 25	Incident Rain	18.5	0.019	0.028	0.100	0.011	0.028	5.44	
	Throughfall		0.025	0.377	0.198	0.040	0.143	5.46	0.226
	Stemflow		0.001	0.004	0.003	0.001	0.006	4.59	0.004
September 8	Incident Rain	101.6	0.091	0.041	0.203	0.020	0.000	5.47	
	Throughfall		0.118	0.660	0.370	0.077	0.388	5.24	4.595
	Stemflow		0.004	0.059	0.125	0.018	0.122	4.39	0.354
October 10	Incident Rain	31.8	0.032	0.025	0.146	0.013	-	5.20	
	Throughfall		0.059	1.007	0.302	0.066	-	5.57	-
	Stemflow		0.000	0.004	0.006	0.001	-	4.22	-

10.4 PRINCIPAL COMPONENT ANALYSIS

The results of principal component analyses of jack pine and trembling aspen throughfall data are shown in the following tables. This procedure was performed in order to determine whether there were differences in the factors associated with the leaching of cations from the tree crowns at the control site as compared to the site exposed to sulphur dioxide. Such a distinction would allow hypotheses to be proposed regarding the mechanisms causing increased leaching of nutrients at the exposed site.

The process of factor analysis or principal component analysis involved three steps[1]:

1. Preparation of the correlation matrix;

2. Extraction of the initial factors--the exploration of possible data reduction; and

3. Rotation to a terminal solution--the search for simple and interpretable factors.

The first step in factor analysis involves the

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[1] The following discussion is largely taken from the Statistical Package for the Social Sciences (SPSS) Manual (Nie *et al.* 1975). The reader is directed to that publication for further details on the process of principal component analysis.

calculation of appropriate measures of association (in this case correlation coefficients) for a set of relevant variables. The variables used for this analysis were H^+, Na^+, K^+, Ca^{++}, Mg^{++} and $SO_4^{=}$-S concentrations, titratable acidity and pH.

The second step constructs a set of new variables on the basis of the interrelations exhibited in the data. The new variables are defined as exact mathematical transformations of the original data--this is known as principal component analysis. The factors are extracted in such a way that one factor is independent from the other i.e. they are orthogonal to each other. In this process no particular asumption about the underlying structure of the variables is required. This procedure determines the particular combination of variables which account for more of the variance in the data as a whole than any other linear combination of variables. The first principal component, therefore, may be viewed as the single best summary of linear relationships exhibited in the data. The second component is defined as the second best linear combination of variables, under the condition that the second component is orthogonal to the first. Subsequent components are defined similarly until all the variance in the data is exhausted.

The factors produced by this process may or may not give a more meaningful pattern of variables. By a process of

rotating the factors it is possible to simplify the factor matrix. This process is presented in the following tables as the varimax rotated factor matrix. The coefficients in the table represent both regression weights and correlation coefficients. The numbers in a given row represent regression coefficients of factors to describe a given variable. For example, in the first table, the most important determinant of H+ concentration is Factor 2, and the influence of the other factors is negligible. In addition, the importance of a given factor for a given variable can be expressed exactly in terms of the variance in the variable that can be accounted for by the factor.

In this case the variance of H+ concentration accounted for by the variance in Factor 2 is given by:

$$\text{variance} = (-0.87)^2 = 0.76$$

That is 76 per cent of the total variance of H+ concentration is accounted for by Factor 2.

In this manner it is possible to reduce the data to a smaller set of factors or components. It is then up to the author to interpret the factor pattern and the cause of any underlying pattern of relationships.

Table 46. Control aspen throughfall-principal component analysis.

Variables	Mean	Standard Deviation	Number of Cases
H+	0.00	0.00	43
Volume (ml)	1712.44	1362.18	43
Na+	0.10	0.03	43
K+	1.22	0.64	43
Ca++	0.94	0.39	43
Mg++	0.15	0.08	43
pH	6.27	0.43	43
Titratable acidity (TA)	0.95	1.02	43
SO4=-S	0.36	0.25	43

Correlation Coefficients	H+	Volume	Na+	K+	Ca++	Mg++	pH	TA	SO4=-S
H+	1.00	0.09	-0.23	-0.60	-0.41	-0.47	0.83	0.21	-0.20
Volume	0.09	1.00	-0.34	-0.12	-0.46	-0.29	0.24	0.90	-0.43
Na+	-0.23	-0.34	1.00	0.07	0.52	0.59	0.27	-0.33	0.59
K+	-0.60	-0.12	0.07	1.00	0.31	0.43	0.76	-0.17	0.13
Ca++	-0.41	-0.46	0.52	0.31	1.00	0.93	0.44	-0.39	0.74
Mg++	-0.47	-0.29	0.59	0.43	0.93	1.00	0.53	-0.25	0.69
pH	-0.83	-0.24	0.27	0.76	0.44	0.53	1.00	-0.37	0.19
TA=	0.21	-0.90	-0.33	-0.17	-0.39	-0.25	-0.37	1.00	-0.35
SO4=-S	-0.20	-0.43	0.59	0.13	0.74	0.69	0.19	-0.35	1.00

Varimax Rotated Factor Matrix[1]	Factor 1	Factor 2	Factor 3
Variance %[2]	48.7	20.5	14.7
H+	-0.20	-0.87	0.02
Volume	-0.27	-0.03	0.94
Na+	0.75	0.04	-0.19
K+	0.07	0.87	-0.05
Ca++	0.85	0.30	-0.21
Mg++	0.86	0.41	-0.03
pH	0.18	0.92	-0.19
TA=	-0.18	-0.17	0.95
SO4=-S	0.87	0.01	-0.21

[1] The numbers in a given row represent the regression coefficients of factors to describe a given variable. The per cent of the variance in the variable that can be accounted for by the factor is equal to the square of each value

[2] Per cent of total data variance (all variables) accounted for by a given factor

Table 47. Exposed aspen throughfall-principal component analysis.

Variables	Mean	Standard Deviation	Number of Cases
H+	0.00	0.00	38
Volume (ml)	1434.34	1090.83	38
Na+	0.11	0.04	38
K+	1.41	0.67	38
Ca++	2.24	2.14	38
Mg++	0.22	0.09	38
pH	6.60	0.32	38
Titratable acidity (TA)	0.53	0.42	38
SO4=-S	0.82	0.25	38

Correlation Coefficients

	H+	Volume	Na+	K+	Ca++	Mg++	pH	TA	SO4=-S
H+	1.00	-0.24	0.02	-0.39	-0.29	-0.27	-0.91	0.14	-0.27
Volume	-0.23	1.00	-0.68	-0.24	0.45	-0.59	0.32	0.43	-0.24
Na+	-0.02	-0.68	1.00	0.36	-0.24	0.51	-0.06	-0.44	0.10
K+	-0.39	-0.24	0.36	1.00	0.20	0.71	0.51	-0.40	0.13
Ca++	-0.29	0.45	-0.24	0.20	1.00	0.01	0.36	0.08	-0.08
Mg++	-0.27	-0.59	0.51	0.71	0.01	1.00	0.33	-0.54	0.41
pH	-0.91	0.32	-0.06	0.51	0.36	0.33	1.00	-0.29	0.24
TA=	0.14	0.43	-0.44	-0.40	0.08	-0.54	-0.29	1.00	-0.23
SO4=-S	-0.27	-0.24	0.10	0.14	-0.09	0.41	0.24	-0.23	1.00

Varimax Rotated Factor Matrix[1]

	Factor 1	Factor 2	Factor 3
Variance %[2]	36.8	28.1	11.2
H+	-0.06	-0.87	0.23
Volume	-0.77	0.46	0.27
Na+	0.81	-0.21	-0.03
K+	0.69	0.51	0.14
Ca++	-0.12	0.60	0.49
Mg++	0.84	0.27	-0.22
pH	0.12	0.94	-0.13
TA=	-0.70	-0.16	0.12
SO4=-S	0.16	0.22	-0.86

[1] The coefficients in this table represent both regression weights and correlation coefficients. The numbers in a given row represent regression coefficients of factors to describe a given variable. In addition, the percent of the variance in the variable that can be accounted for by the factor is equal to the square of each value.
[2] Per cent of total data variance (all variables) accounted for by a given factor.

Table 48. Control pine throughfall-principal component analysis.

Variables	Mean	Standard Deviation	Number of Cases
H+	0.00	0.00	47
Volume (ml)	1750.19	1427.61	47
Na+	0.18	0.07	47
K+	0.72	0.52	47
Ca++	1.31	0.75	47
Mg++	0.32	0.24	47
pH	5.16	0.23	47
Titratable acidity (TA)	2.07	1.76	47
SO4=-S	0.70	0.58	47

Correlation Coefficients

	H+	Volume	Na+	K+	Ca++	Mg++	pH	TA	SO4=-S
H+	1.00	-0.47	0.07	0.20	0.30	0.17	-0.96	-0.17	0.35
Volume	-0.47	1.00	0.27	-0.29	-0.18	-0.03	0.47	0.84	-0.34
Na+	0.07	0.27	1.00	0.66	0.74	0.84	-0.09	0.50	0.70
K+	0.20	-0.29	0.66	1.00	0.73	0.69	-0.24	0.00	0.79
Ca++	0.30	-0.18	0.74	0.73	1.00	0.92	-0.33	0.20	0.94
Mg++	0.17	-0.03	0.84	0.69	0.92	1.00	-0.21	0.34	0.91
pH	-0.96	0.47	-0.09	-0.24	-0.33	-0.21	1.00	0.13	-0.38
TA=	-0.17	0.84	0.50	0.00	0.20	0.34	0.13	1.00	-0.04
SO4=-S	0.35	-0.34	0.70	0.79	0.94	0.91	-0.39	0.04	1.00

Varimax Rotated Factor Matrix[1]

	Factor 1	Factor 2	Factor 3
Variance %[2]	50.0	29.1	13.6
H+	0.12	0.97	-0.15
Volume	-0.15	-0.34	0.92
Na+	0.84	0.01	0.42
K+	0.86	0.05	-0.19
Ca++	0.93	0.20	0.03
Mg++	0.94	0.09	0.18
pH	-0.17	0.97	0.14
TA=	0.18	0.04	0.96
SO4=-S	0.94	0.22	-0.13

[1] The coefficients in this table represent both regression weights and correlation coefficients. The numbers in a given row represent regression coefficients of factors to describe a given variable. In addition, the percent of the variance in the variable that can be accounted for by the factor is equal to the square of each value.
[2] Per cent of total data variance (all variables) accounted for by a given factor.

Table 49. Exposed pine throughfall-principal component analysis.

Variables	Mean	Standard Deviation	Number of Cases
H^+	0.00	0.00	46
Volume (ml)	1306.20	1254.52	46
Na^+	0.23	0.29	46
K^+	2.03	2.66	46
Ca^{++}	2.79	7.25	46
Mg^{++}	0.91	3.24	46
pH	4.83	0.40	46
Titratable acidity (TA)	3.11	1.86	46
$SO_4^{=}$-S	2.17	5.35	46

Correlation Coefficients

	H^+	Volume	Na^+	K^+	Ca^{++}	Mg^{++}	pH	TA	$SO_4^{=}$-S
H^+	1.00	-0.29	0.96	0.92	0.89	0.89	-0.81	0.34	0.93
Volume	-0.29	1.00	-0.32	-0.39	-0.25	-0.20	0.34	0.47	-0.24
Na^+	0.96	-0.32	1.00	0.95	0.95	0.96	-0.67	0.21	0.98
K^+	0.92	-0.39	0.95	1.00	0.91	0.92	-0.68	0.22	0.93
Ca^{++}	-0.89	-0.25	0.95	0.91	1.00	0.99	-0.50	0.13	0.99
Mg^{++}	0.89	-0.21	0.96	0.92	0.99	1.00	-0.51	0.18	0.99
pH	-0.81	0.34	-0.67	-0.68	-0.50	-0.51	1.00	-0.52	-0.58
TA=	0.34	0.47	0.21	0.22	0.13	0.18	-0.52	1.00	0.19
$SO_4^{=}$-S	0.93	-0.24	0.98	0.93	0.99	0.99	-0.58	0.19	1.00

Varimax Rotated Factor Matrix[1]

	Factor 1	Factor 2
Variance %[2]	70.5	16.9
H^+	0.98	0.06
Volume	-0.32	0.78
Na^+	0.99	-0.06
K^+	0.97	-0.08
Ca^{++}	0.95	-0.10
Mg^{++}	0.96	-0.05
pH	-0.23	-0.23
TA=	0.29	0.91
$SO_4^{=}$-S	0.97	-0.05

[1] The coefficients in this table represent both regression weights and correlation coefficients. The numbers in a given row represent regression coefficients of factors to describe a given variable. In addition, the percent of the variance in the variable that can be accounted for by the factor is equal to the square of each value.
[2] Per cent of total data variance (all variables) accounted for by a given factor.

Table 50. Control aspen stemflow - principal component analysis.

Variables	Mean	Standard Deviation	Number of Cases
DBH	18.91	5.03	50
H+	0.00	0.00	50
Volume (ml)	15732.40	8609.67	50
Na+	0.13	0.04	50
K+	2.69	0.85	50
Ca++	9.27	3.89	50
Mg++	1.28	0.55	50
pH	7.57	0.20	50
SO4=-S	0.67	0.53	50

Correlation Coefficients

	DBH	H+	Volume	Na+	K+	Ca++	Mg++	pH	SO4=-S
DBH	1.00	0.27	0.44	-0.26	-0.05	-0.37	-0.21	-0.30	-0.25
H+	0.27	1.00	0.17	-0.23	-0.25	-0.54	-0.53	-0.91	-0.44
Volume	0.44	0.17	1.00	-0.22	-0.49	-0.54	-0.48	-0.17	-0.75
Na+	-0.26	-0.23	-0.22	1.00	0.47	0.47	0.50	0.21	0.35
K+	-0.05	-0.25	-0.49	0.47	1.00	0.66	0.72	0.31	0.73
Ca++	-0.37	-0.54	-0.54	0.47	0.66	1.00	0.96	0.65	0.73
Mg++	-0.21	-0.53	-0.48	0.50	0.72	0.96	1.00	0.62	0.73
pH	-0.30	-0.91	-0.17	0.21	0.31	0.65	0.62	1.00	0.48
SO4=-S	-0.25	-0.44	-0.75	0.35	0.76	0.73	0.73	0.48	1.00

Varimax Rotated Factor Matrix[1]

	Factor 1	Factor 2	Factor 3
Variance %[2]	54.0	15.4	11.8
DBH	-0.03	-0.23	0.91
H+	-0.18	-0.93	0.11
Volume	-0.63	0.09	0.64
Na+	0.57	0.12	-0.09
K+	0.91	0.09	0.06
Ca++	0.76	0.49	-0.23
Mg++	0.82	0.47	-0.07
pH	0.24	0.94	-0.11
SO4=-S	0.82	0.24	-0.28

[1] The coefficients in this table represent both regression weights and correlation coefficients. The numbers in a given row represent regression coefficients of factors to describe a given variable. In addition, the percent of the variance in the variable that can be accounted for by the factor is equal to the square of each value.

[2] Per cent of total data variance (all variables) accounted for by a given factor.

Table 51. Exposed aspen stemflow - principal component analysis.

Variables	Mean	Standard Deviation	Number of Cases
DBH	14.37	5.07	41
H+	0.00	0.00	41
Volume (ml)	10443.90	7533.86	41
Na+	0.15	0.09	41
K+	3.86	1.08	41
Ca++	20.26	7.57	41
Mg++	2.52	1.30	41
pH	7.92	0.31	41
SO4=-S	2.61	1.28	41

Correlation Coefficients

	DBH	H+	Volume	Na++	K+	Ca++	Mg++	pH	SO4=-S
DBH	1.00	0.25	0.65	-0.19	0.20	-0.20	-0.14	-0.13	-0.27
H+	0.25	1.00	0.26	-0.13	-0.09	-0.44	-0.39	-0.87	-0.39
Volume	0.65	0.26	1.00	-0.41	-0.00	-0.12	-0.15	-0.19	-0.27
Na+	-0.19	-0.13	-0.41	1.00	0.12	0.25	0.13	-0.07	0.52
K+	0.20	-0.09	-0.00	0.12	1.00	0.64	0.68	0.12	0.59
Ca++	-0.20	-0.44	-0.12	0.25	0.64	1.00	0.89	0.34	0.75
Mg++	-0.14	-0.39	-0.15	0.13	0.68	0.89	1.00	0.30	0.72
pH	-0.13	-0.87	-0.19	0.07	0.12	0.34	0.30	1.00	0.27
SO4=-S	-0.27	-0.39	-0.27	0.52	0.59	0.75	0.72	0.27	1.00

Varimax Rotated Factor Matrix[1]

	Factor 1	Factor 2	Factor 3
Variance %[2]	42.7	20.6	15.9
DBH	0.06	0.81	-0.20
H+	-0.21	0.17	-0.92
Volume	-0.02	0.86	-0.15
Na+	0.31	-0.63	-0.13
K+	0.87	0.16	-0.05
Ca++	0.87	-0.13	0.28
Mg++	0.88	-0.07	0.25
pH	0.14	-0.04	0.94
SO4=-S	0.82	-0.38	0.14

[1] The coefficients in this table represent both regression weights and correlation coefficients. The numbers in a given row represent regression coefficients of factors to describe a given variable. In addition, the percent of the variance in the variable that can be accounted for by the factor is equal to the square of each value.
[2] Per cent of total data variance (all variables) accounted for by a given factor.

Table 52. Control pine stemflow - principal analysis.

Variables	Mean	Standard Deviation	Number of Cases
Titratable acidity (TA)	22.26	34.57	43
H^+	0.00	0.00	43
Volume (ml)	3732.09	5697.93	43
Na^+	0.51	0.37	43
K^+	2.02	1.24	43
Ca^{++}	10.55	12.27	43
Mg^{++}	1.84	1.85	43
pH	4.81	0.52	43
$SO_4^{=}$-S	5.71	11.17	43

Correlation Coefficients

	TA	H^+	Volume	Na^{++}	K^+	Ca^{++}	Mg^{++}	pH	$SO_4^{=}$-S
TA	1.00	0.34	0.87	-0.01	-0.09	-0.10	-0.18	-0.35	-0.03
H^+	0.34	1.00	0.12	0.31	0.33	0.18	0.31	-0.79	0.21
Volume	0.87	0.12	1.00	-0.18	-0.25	-0.23	-0.34	-0.21	-0.15
Na^+	-0.01	0.31	-0.18	1.00	0.91	0.91	0.75	-0.24	0.90
K^+	-0.09	0.33	-0.25	0.91	1.00	0.83	0.72	-0.25	0.81
Ca^{++}	-0.10	0.18	-0.23	0.91	0.83	1.00	0.56	-0.05	0.97
Mg^{++}	-0.18	0.31	-0.34	0.75	0.72	0.56	1.00	-0.15	0.46
pH	-0.35	0.31	-0.34	0.75	0.72	0.56	1.00	0.15	0.46
$SO_4^{=}$-S	-0.03	0.21	-0.15	0.90	0.81	0.97	0.46	-0.18	1.00

Varimax Rotated Factor Matrix[1]

	Factor 1	Factor 2	Factor 3
Variance %[2]	49.1	26.2	13.0
TA	-0.02	0.92	0.26
H^+	0.17	0.11	0.92
Volume	-0.16	0.95	0.07
Na^+	0.96	-0.07	0.21
K^+	0.89	-0.16	0.26
Ca^{++}	0.97	-0.07	-0.01
Mg^{++}	0.61	-0.39	0.35
pH	-0.11	-0.19	-0.90
$SO_4^{=}$-S	-0.96	0.04	0.03

[1] The coefficients in this table represent both regression weights and correlation coefficients. The numbers in a given row represent regression coefficients of factors to describe a given variable. In addition, the percent of the variance in the variable that can be accounted for by the factor is equal to the square of each value.

[2] Per cent of total data variance (all variables) accounted for by a given factor.

Table 53. Exposed pine stemflow - principal component analysis.

Variables	Mean	Standard Deviation	Number of Cases
Titratable Acidity (TA)	115.21	157.43	37
H+	0.00	0.00	37
Volume (ml)	6170.67	8766.88	37
Na+	0.72	0.36	37
K+	9.24	4.53	37
Ca++	14.30	11.23	37
Mg++	4.15	3.16	37
pH	3.62	0.20	37
SO4=-S	2.08	13.12	37

Correlation Coefficients

	TA	H+	Volume	Na++	K+	Ca++	Mg++	pH	SO4=-S
TA	1.00	-0.31	0.71	-0.48	-0.44	-0.35	-0.41	0.37	-0.46
H+	-0.31	1.00	-0.64	0.70	0.71	0.23	0.72	-0.97	0.73
Volume	0.71	-0.64	1.00	-0.74	-0.74	-0.54	-0.61	0.75	-0.71
Na+	-0.48	0.70	-0.74	1.00	0.78	0.37	0.73	-0.74	0.73
K+	-0.44	0.71	-0.74	0.78	1.00	0.47	0.68	-0.75	0.73
Ca++	-0.35	0.23	-0.54	0.37	0.47	1.00	0.43	-0.35	0.69
Mg++	-0.41	0.72	-0.61	0.73	0.68	0.43	1.00	-0.71	0.91
pH	0.37	-0.97	0.75	-0.74	-0.75	-0.35	-0.71	1.00	-0.77
SO4=-S	-0.46	0.73	-0.71	0.73	0.73	0.69	0.91	-0.77	1.00

Varimax Rotated Factor Matrix[1]

	Factor 1	Factor 2
Variance %[2]	67.2	11.6
TA	-0.59	0.53
H+	0.84	-0.46
Volume	-0.87	0.24
Na+	0.87	0.10
K+	0.87	0.05
Ca++	0.58	-0.59
Mg++	0.86	0.12
pH	-0.89	-0.34
SO4=-S	0.92	-0.06

[1] The coefficients in this table represent both regression weights and correlation coefficients. The numbers in a given row represent regression coefficients of factors to describe a given variable. In addition, the percent of the variance in the variable that can be accounted for by the factor is equal to the square of each value.
[2] Per cent of total data variance (all variables) accounted for by a given factor.

10.5 JACK PINE STEMFLOW EXPERIMENT - ANALYSIS OF VARIANCE

The tables below present the results of a one way analysis of variance of pH, titratable acidity and $SO_4^{=}$-S concentrations of jack pine stemflow; and of the total sulphation by site. Total sulphation was expressed as mg SO_3 equivalent/100 cm^2 sulphation plate area/day. Data from this experiment are represented in Table 28 in the text.

Table 54. One way analysis of variance of the pH of jack pine stemflow by site.

Source of Variation	Sum of Squares	df	Mean Square	F-Value
Between Groups	5.0148	3	1.6716	6.716***
Within Groups	12.4451	50	0.2489	
Total	17.4598	53		

***significant at $p < 0.001$

Table 55. One way analysis of variance of the titratable acidity of jack pine stemflow by site

Source of Variation	Sum of Squares	df	Mean Square	F-Value
Between Groups	1.8544	3	0.6181	2.903*
Within Groups	10.6456	50	0.2129	
Total	12.5001	53		

*significant at $p < 0.05$

Table 56. One way analysis of variance of the SO4=-S concentrations of jack pine stemflow by site

Source of Variation	Sum of Squares	df	Mean Square	F-Value
Between Groups	2269.0292	3	756.3430	14.572***
Within Groups	2595.1317	50	51.9026	
Total	4864.1602	53		

***significant at $p < 0.001$

Table 57. One way analysis of variance of total sulphation (mg SO3 equivalent/cm²/day) by site

Source of Variation	Sum of Squares	df	Mean Square	F-Value
Between Groups	0.0261	3	0.0087	27.204***
Within Groups	016351	51	0.0003	
Total	0.0425	54		

***significant at $p < 0.001$

10.6 COMPARISON OF THE RATIOS OF IONS IN RAINWATER AND TREMBLING ASPEN AND JACK PINE THROUGHFALL

The ratios of ions in rainwater and in throughfall were calculated for both species at both the control site and the exposed site. By combining the ratios of calcium to the other ions (Tables 23 and 24) and magnesium to the other ions (Tables 58 and 59) the relative removal of the various nutrients at each site can be determined.

Table 58. Increases in the ratio of ions relative to magnesium due to the forest canopy of trembling aspen. Ratios were calculated from the concentrations in meq/1 (After Attiwill 1966).

Date	Mg^{++}/Na^{+}			Mg^{++}/K^{+}			Mg^{++}/Ca^{++}			$Mg^{++}/SO_4^{=}$-S		
	o	uc	i	o	uc	i	o	uc	i	o	uc	i
Control Site												
29 June	0.47	2.54	-19.22	0.59	0.55	0.17	0.09	0.22	0.21	0.21	0.62	0.45
16 July	1.14	2.58	9.03	0.84	0.45	0.11	0.25	0.27	0.18	0.83	0.87	0.34
23 July	0.56	4.22	-0.37	0.57	0.51	0.14	0.26	0.28	0.18	1.46	1.04	0.30
30 July	3.41	1.29	-3.91	8.28	0.48	-0.19	0.63	0.24	-0.78	5.93	2.15	-4.05
27 Aug.	1.01	2.89	-0.30	3.68	0.39	0.03	0.33	0.32	0.17	-	1.66	0.15
9 Sept.	0.95	2.76	-1.86	2.76	0.25	0.04	0.24	0.29	0.22	0.63	1.41	-3.88
2 Oct.	0.76	2.50	-17.83	1.61	0.22	0.05	0.18	0.31	0.28	-	-	-
Mean			-2.77			0.05			0.03			-1.12
Exposed Site												
30 June	0.49	3.09	-0.34	0.74	0.50	0.12	0.22	0.24	0.16	0.55	0.69	0.36
15 July	0.33	3.65	-0.58	0.61	0.42	0.11	0.15	0.22	0.17	0.18	1.54	-0.25
29 July	1.26	3.52	-9.30	1.93	0.57	0.12	0.20	0.20	0.12	1.58	0.96	0.29
10 Aug.	2.16	3.60	3.08	1.36	0.40	0.09	2.64	0.26	0.10	1.41	1.85	0.86
8 Sept.	0.63	3.34	15.20	2.15	0.37	0.10	0.16	0.06	0.03	0.19	1.13	-15.33
10 Oct.	1.68	36.66	75.11	3.22	0.50	0.15	0.31	0.45	0.28	-	-	-
Mean			1.61			0.11			0.12			-2.81

Table 59. Increases in the ratio of ions relative to magnesium due to the forest canopy of jack pine. Ratios were calculated from the concentrations in meq/1 (After Attiwill 1966).

Date	Mg^{++}/Na^{+}			Mg^{++}/K^{+}			Mg^{++}/Mg^{++}			$Mg^{++}/SO_4^{=}$-S		
	o	uc	i	o	uc	i	o	uc	i	o	uc	i
Control Site												
29 June	1.26	2.98	2.83	2.41	1.15	0.31	0.19	0.34	0.27	0.63	0.91	0.40
16 July	0.42	3.87	4.59	0.64	1.29	0.43	0.16	0.42	0.29	0.28	0.91	0.41
23 July	1.16	3.08	5.72	2.57	1.17	0.29	0.21	0.37	0.35	0.75	0.70	0.26
27 Aug.	0.95	3.91	3.43	2.57	1.67	0.50	0.15	0.41	0.32	1.05	1.72	0.71
9 Sept.	0.15	2.44	62.04	0.46	1.98	0.78	0.10	0.48	0.38	-	2.17	0.77
2 Oct.	0.76	4.07	11.42	1.84	1.99	0.63	0.19	0.45	0.36	-	1.85	0.59
Mean			15.72			0.46			0.32			0.51
Exposed Site												
30 June	0.49	7.33	-9.67	0.74	1.79	0.65	0.22	0.62	0.46	0.55	1.02	0.42
15 July	0.33	3.64	-3.23	0.61	0.72	0.23	0.15	0.47	0.42	0.18	0.82	0.74
29 July	1.26	3.51	9.44	1.93	0.56	0.13	0.20	0.40	0.44	1.58	0.66	0.20
10 Aug.	-	4.42	-	-	0.77	-	-	0.19	-	-	1.07	-
25 Aug.	2.16	4.04	4.73	1.36	0.69	0.16	0.26	0.38	0.31	1.41	0.79	0.24
8 Sept.	0.63	1.69	3.27	2.15	0.52	0.12	0.16	0.32	0.32	0.19	0.42	0.35
10 Oct.	1.68	2.68	2.95	3.22	0.22	0.04	0.31	0.35	0.24	-	-	-
Mean			0.91			0.26			0.39			0.39

10.7 PHOTOGRAPHS OF THE SIX STUDY PLOTS USED IN THE NUTRIENT CYCLING STUDY, 1976

Plate 2. Control trembling aspen plot. Note the throughfall gauges and stemflcw collection gauge.

Plate 3. Exposed trembling aspen plot. Note the throughfall gauges and one of the litter traps.

Plate 4. Control jack pine plot.

Plate 5. Exposed jack pine plot

Plate 6. Control black spruce plot.

Plate 7. Exposed black spruce plot. Note the dense nature of the stand and the small size of the trees.